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[US/US]; 3505 Sage Road #810, Houston, Texas 77056  
(US).

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(74) Agent: **VANDE GUCHT, Anne; SOLVAY (Société Anonyme), Intellectual Property Department, Rue de Ransbeek, 310, B-1120 Bruxelles (BE).**

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(71) Applicant (for all designated States except US): **SOLVAY (Société Anonyme) [BE/BE]**; Rue du Prince Albert, 33, B-1050 Bruxelles (BE).

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(72) Inventors; and

(75) Inventors/Applicants (for US only): **KRAFFT, Philippe** [FR/BE]; Avenue Simonne, 21A, B-1640 Rhode Saint Genèse (BE). **GILBEAU, Patrick** [BE/BE]; Chemin de la Fontenelle, 20, B-7090 Braine-le-Comte (BE). **BALTHASART, Dominique** [BE/BE]; Rue du Château Beyard, 150, B-1120 Brussels (BE). **BOULOS, Noël**

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(54) Title: EPICHLOROHYDRIN, MANUFACTURING PROCESS AND USE

(57) Abstract: Product containing epichlorohydrin, wherein the amount of trichloropropane is of less than 0.01 g of trichloropropane per kg of product, a process for manufacturing the product and its use in various applications.

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Epichlorohydrin, manufacturing process and use

The present patent application claims the benefit of the French Patent applications FR 07/55696 filed on 12 June 2007, FR 07/57751 filed on 21 September 2007, of the United States Provisional Patent Application USP 61/013672 filed on 14 December 2007 and of the United States Provisional Patent Application USP 61/007661 filed on 14 December 2007 the content of all of which is incorporated herein by reference.

The present invention relates to an epichlorohydrin-based product, to a process for the manufacture and purification thereof and to the use of the product in various manufactures.

10 Epichlorohydrin is a reaction intermediate in the manufacture of epoxy resins, synthetic elastomeres, glycidyl ethers, polyamide resins, etc. (Ullmann's Encyclopedia of Industrial Chemistry, Fifth Edition, Vol. A9, p.539). The epichlorohydrin can be manufactured, for instance, by dehydrochlorination of dichloropropanol derived from hypochlorination of allyl chloride. The 15 epichlorohydrin thus obtained is not suitable for certain applications.

The object of the present invention is to provide a product containing epichlorohydrin which does not have these disadvantages.

20 The invention hence relates to a product containing epichlorohydrin and trichloropropane, wherein the amount of trichloropropane is of less than 0.01 g of trichloropropane per kg of product.

One of the essential characteristics of the invention resides in the low 25 amount of trichloropropane present in the epichlorohydrin product. The presence of trichloropropane amongst other halogenated hydrocarbons in epichlorohydrin have indeed proven troublesome in some of the applications, such as for example, in manufacturing epoxy resins intended for the electrical component and printed circuit industry. Some halogenated hydrocarbons, among which trichloropropane, for instance are or are suspected to be carcinogenic, are suspected to have development toxicity, reproductive toxicity, cardiologic toxicity, endocrine toxicity, immunotoxicity and toxicity to the liver, the 30 kidneys, the nerves, the respiratory tract and to the skin. They can remain in the final products and possibly degrade with a concomitant deterioration of the properties of the final products. They can exhibit or degrade in compounds

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exhibiting some toxicity leading to safety issues especially when the final products are intended to be in contact with food and drink. Moreover, they can accumulate in and contaminate industrial waters such as wastewaters for instance or water containing pulp that is recycled in the pulp and paper industry. In the 5 latter case, their higher concentration can increase contamination of the paper made using the recycled water.

The epichlorohydrin content in the product is generally greater than 900 g of epichlorohydrin per kg of product, preferably at least 950 g/kg, more preferably at least 990 g/kg and most particularly preferably at least 999 g/kg.

10 The trichloropropane in the product according to the invention is present, in an amount of generally less than or equal to 0.008 g/kg of product, often of less than or equal to 0.006 g/kg, frequently of less than or equal to 0.004 g/kg, commonly of less than or equal to 0.002 g/kg, in many cases of less than or equal to 0.001 g/kg, and particularly of less than or equal to 0.0005 g/kg. That content 15 is usually of at least 0.001 mg/kg.

The trichloropropane may be selected from any isomer of trichloropropane, alone or in combination, and the content of TCPa in the product according to the invention refers to the sum of all the isomers.

20 The trichloropropane can be selected from 1,2,3-trichloropropane, 1,1,1-trichloropropane, 1,1,3-trichloropropane, 1,1,2-trichloropropane and any mixtures of at least two of them. The trichloropropane is often 1,1,1-trichloropropane.

25 The product according to the invention may contain in addition to trichloropropane and epichlorohydrin, at least one halogenated hydrocarbon different from trichloropropane. That halogenated hydrocarbon can be chosen from chloropropene, trichloropropene, chloropropanol, chloropropenol, dichloropropene, dichloropropane, dichloropropanol, monochloropropanediol, chloroethers, monochlorobenzene, and any mixture of at least two of them.

30 The content of that halogenated hydrocarbon in the product is usually of less than 1 g/kg of product, commonly less than or equal to 0.8 g/kg of product, usually less than or equal to 0.6 g/kg, in many cases less than or equal to 0.5 g/kg, often less than or equal to 0.4 g/kg, frequently less than or equal to 0.2 g/kg, more often less than or equal to 0.1 g/kg, more frequently less than or equal to 0.05 g/kg, in particular less than or equal to 0.01 g/kg, and specifically less than or equal to 0.001 g/kg. This content is generally greater than or equal to 0.001 mg/kg.

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The halogenated hydrocarbon may be an aliphatic or an aromatic halogenated hydrocarbon, optionally containing oxygen, preferably an aliphatic halogenated hydrocarbon, such as:

- chloropropene, often 2-chloro-1-propene, frequently 1-chloro-1-propene cis,  
5 usually 1-chloro-1-propene trans, specifically 3-chloro-1-propene, and any mixture of at least two of them
- chloropropane, often 2-chloropropane, frequently 1-chloropropane, and any mixture of at least two of them
- chloromethane, often dichloromethane, frequently trichloromethane, usually  
10 tetrachloromethane, and any mixture of at least two of them
- dichloroethane, often 1,2-dichloroethane,
- chloroethanol, often 2-chloroethanol,
- trichloropropene, often 1,3,3-trichloro-1-propene-cis, frequently 1,3,3-trichloro-1-propene-trans, usually 1,2,3-trichloropropene-cis, specifically  
15 1,2,3-trichloropropene-trans, and any mixture of at least two of them
- chloropropanol, often 3-chloro-1-propanol,
- chloropropenol, often 2-chloro-2-propen-1-ol, frequently 3-chloro-2-propen-1-ol cis and specifically 3-chloro-2-propene-1-ol trans, and any mixture of at least two of them  
20
- dichloropropene, often cis-1,3-dichloropropene, frequently trans-1,3-dichloropropene, usually 3,3-dichloro-1-propene, frequently 2,3-dichloro-1-propene, usually 1,3-dichloro-1-propene-cis, specifically 1,3-dichloro-1-propene-trans, and any mixture of at least two of them,
- dichloropropane, preferably 1,3-dichloropropane, 1,2-dichloropropane, 2,2-dichloropropane, and any mixture thereof  
25
- dichloropropanol, often 1,3-dichloropropan-2-ol, 2,3-dichloropropan-1-ol, and mixtures thereof,
- monochloropropanediol, often 3-chloro-1,2-propanediol, frequently 2-chloro-1,3-propanediol, and mixtures thereof, and  
30
- chloroethers, preferably chosen from chloroethers of crude formula:  
 $C_6H_{10}Cl_2O_2$ ,  $C_6H_{12}Cl_2O$ ,  $C_6H_9Cl_3O_2$ ,  $C_6H_{11}Cl_3O_2$ , and mixtures of at least two of them,
- of crude formula  $C_4H_7ClO_2$ ,  $C_6H_9Cl_3$ ,  $C_6H_9Cl_3O_2$ ,  $C_9H_{17}Cl_3O_4$ ,  $C_9H_{15}Cl_5O$ ,  
35  $C_3H_3Cl_3$ , and mixtures of at least two of them
- dichloroepoxypropane.

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Haloketones and epichlorohydrin are not considered to be halogenated hydrocarbons.

Aromatic halogenated hydrocarbons comprise at least one ring of aromatic nature and a halogen atom. The halogen atom is preferably directly attached to the aromatic ring. The halogen may be chosen from fluorine, chlorine, bromine, iodine and mixtures thereof. Chlorine is preferred. The aromatic ring may be mononuclear or polynuclear, and is preferably mononuclear. The aromatic halogenated hydrocarbons may be chosen from mono-, di-, tri-, tetra-, penta- and hexachloro- benzenes and/or naphthalenes. Monochlorobenzene is particularly preferred.

Without wishing to be tied to one theoretical explanation, it is believed that monochlorobenzene may come from the process for manufacturing epichlorohydrin, in particular when this is obtained by dehydrochlorination of dichloropropanol. More specifically, it is believed that monochlorobenzene may be present in the dichloropropanol, in particular when this is obtained by a process for chlorinating glycerol using a chlorinating agent containing hydrogen chloride. More specifically still, it is believed that chlorobenzene may be present in the hydrogen chloride, in particular when this comes from another manufacturing process, such as the manufacture of isocyanates, diisocyanates or polyisocyanates, such as for example 4,4-methylenediphenyl diisocyanate (MDI) or toluene diisocyanate (TDI) or hexamethylene-1,6-diisocyanate (HDI).

The product according to the invention can contain chloropropene, in a content usually less than or equal to 0.8 g/kg of product, generally less than or equal to 0.6 g/kg, in many cases less than or equal to 0.5 g/kg, often less than or equal to 0.4 g/kg, commonly less than or equal to 0.2 g/kg, advantageously less than or equal to 0.1 g/kg, particularly less than or equal to 0.05 g/kg, specifically less than or equal to 0.01 g/kg. Values less than or equal to 0.001 g/kg give good results. That content is usually of at least 0.001 mg/kg. The chloropropene may be selected from 2-chloro-1-propene, 1-chloro-1-propene cis, 1-chloro-1-propene trans, 3-chloro-1-propene, and any mixture of at least two of them.

The product according to the invention can contain trichloropropene, in an amount a content usually less than or equal to 0.8 g/kg of product, generally less than or equal to 0.6 g/kg, commonly less than or equal to 0.5 g/kg, in many cases less than or equal to 0.4 g/kg, often less than or equal to 0.2 g/kg, frequently less than or equal to 0.1 g/kg, particularly less than or equal to 0.05 g/kg, specifically less than or equal to 0.01 g/kg. A content of less than or equal

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to 0.001 g/kg gives good results. That content is usually of at least 0.001 mg/kg. The trichloropropene may be selected from 1,3,3-trichloro-1-propene-cis, 1,3,3-trichloro-1-propene-trans, 1,2,3-trichloropropene-cis, specifically 1,2,3-trichloropropene-trans and any mixtures of at least two of them.

5       The product according to the invention can contain chloropropenol, in a content usually less than or equal to 0.8 g/kg of product, generally less than or equal to 0.6 g/kg, in many cases less than or equal to 0.5 g/kg, often less than or equal to 0.4 g/kg, commonly less than or equal to 0.2 g/kg, advantageously less than or equal to 0.1 g/kg, particularly less than or equal to 0.05 g/kg, specifically less than or equal to 0.01 g/kg. Values less than or equal to 0.001 g/kg give good results. That content is usually of at least 0.001 mg/kg. The chloropropenol may be selected from 2-chloro-2-propen-1-ol, 3-chloro-2-propene-1-ol cis, 3-chloro-2-propene-1-ol trans and any mixtures of at least two of them.

10      The product according to the invention may contain dichloropropene, in a content a content usually less than or equal to 0.8 g/kg of product, generally less than or equal to 0.6 g/kg, in many cases less than or equal to 0.5 g/kg, often less than or equal to 0.4 g/kg, commonly less than or equal to 0.2 g/kg, advantageously less than or equal to 0.1 g/kg, particularly less than or equal to 0.05 g/kg, specifically less than or equal to 0.01 g/kg. Values less than or equal to 0.001 g/kg give good results. That content is usually of at least 0.001 mg/kg. The dichloropropene may be selected from 3,3-dichloro-1-propene , 2,3-dichloro-1-propene, 1,3-dichloro-1-propene-cis, 1,3-dichloro-1-propene-trans, and any mixtures of at least two of them.

15      The product according to the invention can contain dichloropropane, in a content usually less than or equal to 0.8 g/kg of product, generally less than or equal to 0.6 g/kg, in many cases less than or equal to 0.5 g/kg, often less than or equal to 0.4 g/kg, commonly less than or equal to 0.2 g/kg, advantageously less than or equal to 0.1 g/kg, particularly less than or equal to 0.05 g/kg, specifically less than or equal to 0.01 g/kg. Values less than or equal to 0.001 g/kg give good results. That content is usually of at least 0.001 mg/kg. The dichloropropane may be selected from 1,3-dichloropropane, 1,2-dichloropropane, 2,2-dichloropropane, and any mixture of at least two of them.

20      The product according to the invention can contain dichloropropanol, in a content usually less than or equal to 0.8 g/kg of product, generally less than or equal to 0.6 g/kg, in many cases less than or equal to 0.5 g/kg, often less than or equal to 0.4 g/kg, commonly less than or equal to 0.2 g/kg, advantageously less

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than or equal to 0.1 g/kg, particularly less than or equal to 0.05 g/kg, specifically less than or equal to 0.01 g/kg. Values less than or equal to 0.001 g/kg give good results. That content is usually of at least 0.001 mg/kg. The dichloropropanol may be selected from 1,3-dichloropropan-2-ol, 2,3-dichloropropan-1-ol and any mixtures thereof.

5       The product according to the invention can contain monochloropropanediol, in a content usually less than or equal to 0.8 g/kg of product, generally less than or equal to 0.6 g/kg, in many cases less than or equal to 0.5 g/kg, often less than or equal to 0.4 g/kg, commonly less than or equal to 0.2 g/kg, advantageously less than or equal to 0.1 g/kg, particularly less than or equal to 0.05 g/kg, specifically less than or equal to 0.01 g/kg. Values less than or equal to 0.001 g/kg give good results. That content is usually of at least 0.001 mg/kg. The monochloropropanediol may be selected from 3-chloro-1,2-propanediol, 2-chloro-1,3-propanediol and any mixtures thereof.

10      The product according to the invention usually can contain chloroethers in a content usually less than or equal to 0.8 g/kg of product, generally less than or equal to 0.6 g/kg, in many cases less than or equal to 0.5 g/kg, often less than or equal to 0.4 g/kg, commonly less than or equal to 0.2 g/kg, advantageously less than or equal to 0.1 g/kg, particularly less than or equal to 0.05 g/kg, specifically less than or equal to 0.01 g/kg. Values less than or equal to 0.001 g/kg give good results. That content is usually of at least 0.001 mg/kg. The chloroethers may be selected from chloroethers of crude formula C<sub>6</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>2</sub>, C<sub>6</sub>H<sub>12</sub>Cl<sub>2</sub>O, C<sub>6</sub>H<sub>9</sub>Cl<sub>3</sub>O<sub>2</sub>, C<sub>6</sub>H<sub>11</sub>Cl<sub>3</sub>O<sub>2</sub>, and any mixtures thereof.

15      The product according to the invention usually contains chlorobenzene, often monochlorobenzene, in an amount in a content usually less than or equal to 0.8 g/kg of product, generally less than or equal to 0.6 g/kg, in many cases less than or equal to 0.5 g/kg, often less than or equal to 0.4 g/kg, commonly less than or equal to 0.2 g/kg, advantageously less than or equal to 0.1 g/kg, particularly less than or equal to 0.05 g/kg, specifically less than or equal to 0.01 g/kg. Values less than or equal to 0.001 g/kg give good results. That content is usually of at least 0.001 mg/kg.

20      The product according to the invention may also contain in addition, compounds which are not halogenated hydrocarbons such as defined above, such as for example :

- 25      • aldehydes, like acetaldehyde, acrolein, isobutanal, isopentanal  
          • alkyl glycidyl ether, like methyl glycidyl ether,

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- ketones, like acetone, chloroacetone, cyclopentanone, 2-butanone, cyclohexanone, 2-methyl-2-cyclopentene-1-one, 3,5-dimethyl-2-cyclohexene-1-one ketone of crude formula C<sub>5</sub>H<sub>10</sub>O, C<sub>6</sub>H<sub>12</sub>O,
- aliphatic alcohols, like isopropanol, allyl alcohol, glycerol,

5     • aromatic alcohols like phenol

- hydroxyketones like hydroxyacetone and

- epoxides different from epichlorohydrin, like propylene oxide, 1,2-epoxyhexane, glycidol,

- hydrocarbons like methylcyclopentane, ethylbenzene,

10     • compounds of crude formula C<sub>6</sub>H<sub>10</sub>O, C<sub>7</sub>H<sub>10</sub>O, C<sub>7</sub>H<sub>14</sub>O<sub>2</sub>, C<sub>6</sub>H<sub>8</sub>O<sub>2</sub>, C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>.

The product according to the invention can contain at least one aldehyde, in a content usually less than or equal to 0.8 g/kg of product, generally less than or equal to 0.6 g/kg, in many cases less than or equal to 0.5 g/kg, often less than or equal to 0.4 g/kg, commonly less than or equal to 0.2 g/kg, advantageously

15     less than or equal to 0.1 g/kg, particularly less than or equal to 0.05 g/kg, specifically less than or equal to 0.01 g/kg. Values less than or equal to 0.001 g/kg give good results. That content is usually of at least 0.001 mg/kg. The aldehyde may be selected from acetaldehyde, acrolein, isobutanal, isopentanal and any mixtures of at least two of them.

20     The product according to the invention can contain acrolein in an amount usually of less than 0.07 g/kg of product, generally at most 0.01 g/kg commonly at most 0.005 g/kg. This content is usually at least 0.001 g/kg.

The product according to the invention can contain at least one alkyl

glycidyl ether, in a content usually less than or equal to 0.8 g/kg of product,

25     generally less than or equal to 0.6 g/kg, in many cases less than or equal to 0.5 g/kg, often less than or equal to 0.4 g/kg, commonly less than or equal to 0.2 g/kg, advantageously less than or equal to 0.1 g/kg, particularly less than or equal to 0.05 g/kg, specifically less than or equal to 0.01 g/kg. Values less than or equal to 0.001 g/kg give good results. That content is usually of at least

30     0.001 mg/kg. The alkyl glycidyl ether may be selected from methyl-, ethyl-, propyl-, butyl glycidyl ethers, and any mixtures of at least two of them.

The product according to the invention can contain methyl glycidyl ether in an amount usually of at most 0.5 g/kg of product, generally at most 0.1 g/kg and commonly at most 0.05 g/kg. This content is usually of at least 0.001 g/kg.

35     The product according to the invention can contain ketones, in a content usually less than or equal to 0.8 g/kg of product, generally less than or equal to

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0.6 g/kg, in many cases less than or equal to 0.5 g/kg, often less than or equal to 0.4 g/kg, commonly less than or equal to 0.2 g/kg, advantageously less than or equal to 0.1 g/kg, particularly less than or equal to 0.05 g/kg, specifically less than or equal to 0.01 g/kg. Values less than or equal to 0.001 g/kg give good

5 results. That content is usually of at least 0.001 mg/kg. The ketones may be selected from acetone, chloroacetone, 2-butanone, cyclopentanone, cyclohexanone, 2-methyl-2-cyclopentene-1-one, 3,5-dimethyl-2-cyclohexene-1-one, ketones of crude formula C<sub>5</sub>H<sub>10</sub>O, C<sub>6</sub>H<sub>12</sub>O, and any mixtures of at least two of them.

10 The product according to the invention can contain cyclopentanone in an amount usually higher than or equal to 0.001 mg/kg, generally higher than or equal to 0.01 mg/kg, commonly higher than or equal to 0.1 mg/kg and in many cases higher than or equal to 0.001 g/kg. That content is usually lower than or equal to 0.5 g/kg, generally lower than or equal to 0.3 g/kg, commonly lower than or equal to 0.1 g/kg, in many cases lower than or equal to 0.05 g/kg, often lower than or equal to 0.01 g/kg and particularly lower than or equal to 0.005 g/kg. That content is usually higher than or equal to 0.001 mg/kg, generally higher than or equal to 0.01 mg/kg, commonly higher than or equal to 0.1 mg/kg, in many cases higher than or equal to 0.5 mg/kg and in particular higher than or equal to 1 mg/kg

15 The product according to the invention can contain chloroacetone in an amount usually of less than 0.05 g/kg of product, generally at most 0.03 g/kg and commonly at most 0.01 g/kg. This content is usually at least 0.001 g/kg

20 The product according to the invention can contain aliphatic alcohols, in a content usually less than or equal to 0.8 g/kg of product, generally less than or equal to 0.6 g/kg, in many cases less than or equal to 0.5 g/kg, often less than or equal to 0.4 g/kg, commonly less than or equal to 0.2 g/kg, advantageously less than or equal to 0.1 g/kg, particularly less than or equal to 0.05 g/kg, specifically less than or equal to 0.01 g/kg. Values less than or equal to 0.001 g/kg give good

25 results. That content is usually of at least 0.001 mg/kg. The aliphatic alcohols may be selected from isopropanol, allyl alcohol, glycerol, and any mixtures of at least two of them.

30 The product according to the invention can contain hydroxyketones, in a content in a content usually less than or equal to 0.8 g/kg of product, generally less than or equal to 0.6 g/kg, in many cases less than or equal to 0.5 g/kg, often less than or equal to 0.4 g/kg, commonly less than or equal to 0.2 g/kg,

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advantageously less than or equal to 0.1 g/kg, particularly less than or equal to 0.05 g/kg, specifically less than or equal to 0.01 g/kg. Values less than or equal to 0.001 g/kg give good results. That content is usually of at least 0.001 mg/kg. The hydroxyketone is often hydroxyacetone.

5       The product according to the invention can contain epoxides different from epichlorohydrin, in a content usually less than or equal to 0.8 g/kg of product, generally less than or equal to 0.6 g/kg, in many cases less than or equal to 0.5 g/kg, often less than or equal to 0.4 g/kg, commonly less than or equal to 0.2 g/kg, advantageously less than or equal to 0.1 g/kg, particularly less than or  
10      equal to 0.05 g/kg, specifically less than or equal to 0.01 g/kg. Values less than or equal to 0.001 g/kg give good results. That content is usually of at least 0.001 mg/kg. The epoxide may be selected from propylene oxide, 1,2-epoxyhexane, glycidol, and any mixtures of at least two of them.

15      The product according to the invention can contain glycidol in an amount usually of at most 0.5 g/kg of product, generally of at most 0.2 g/kg, frequently of at most 0.10 g/kg of product, commonly of at most 0.05 g/kg of product, often of at most 0.01 g/kg and frequently of at most 0.005 g/kg.

20      The product according to the invention usually contains glycerol, hydroxyacetone and glycidol, of which the sum of the contents is usually less than 0.1 g/kg of product, commonly at most 0.01 g/kg and generally at most 0.005 g/kg. This content is usually at least 0.001 g/kg.

25      The invention also relates to a process for manufacturing a product containing epichlorohydrin, wherein the amount of trichloropropene is of less than 0.01 g of trichloropropene per kg of product, comprising the following steps:

- a) in a liquid reaction medium, a mixture of dichloropropanol containing 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol, in which the 1,3-dichloro-2-propanol content is at least 10 wt%, is reacted with at least one basic compound in order to form epichlorohydrin and at least one salt; and
- b) at least one part of the liquid reaction medium from step a) is subjected to a settling operation in which a first fraction containing most of the epichlorohydrin which was contained in the part of the reaction medium from step a) before the settling operation is separated from a second fraction containing most of the salt which was contained in the part of the reaction medium from step a) before the settling operation; and

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- c) the first fraction separated in step b) is subjected to at least one supplementary treatment chosen from dilution, concentration, evaporation, distillation, stripping, liquid/liquid extraction and adsorption operations, alone or in combination.

5 In the rest of the document the expression "dichloropropanol" will be used to denote the dichloropropanol mixture.

The expression "most of" is understood to mean "half and more than half of", i.e. 50 % by weight or more than 50 % by weight.

10 The halogenated hydrocarbons may especially be produced during the various steps of the dichloropropanol manufacturing process.

The dichloropropanol from step a) of the process according to the invention may be produced, for example, by chlorination of glycerol and/or by hypochlorination of allyl chloride, the allyl chloride being itself produced by chlorination of propylene. The glycerol may be obtained from oil or grease of plant or animal origin. Oil-producing plant or crops are for example corn, cashew nut, oat, palm, lupine, rubber seed, kenaf, calendula, cotton, hemp, soybean, coffee, linseed, hazelnut, euphorbia, pumpkin seed, coriander, mustard, camelina, sesame, crambe, safflower, buffalo gourd, rice, tung oil tree, sunflower, cocoa, peanut, opium poppy, rapeseed, olive tree, piassava, gopher plant, castor bean, bacuri, pecan, jojoba, babassu palm, jatropha, e.g. jatropha Curcas L., Chinese tallow or Tridica Sebifera L., macadamia nut, brazil nut, avocado, coconut, oiticica, buriti palm, pequi, macauba palm and oil palm. Oil-producing algae are for example *Neochloris oleoabundans*, *Scenedesmus dimorphus*, *Euglena gracilis*, *Phaeodactylum tricornutum*, *Pleurochrysis 25 carterae*, *Prymnesium parvum*, *Tetraselmis chui*, *Tetraselmis suecica*, *Isochrysis galbana*, *Nannochloropsis salina*, *Nannochloris atomus* Butcher, *Nannochloris maculata* Butcher, *Nannochloropsis gaditana* Lubian, and *Nannochloropsis oculata*. Algal strains such as *Botryococcus braunii*, *Botryococcus*, *Dunaliella tertiolecta*, *Nannochloris* sp., *Spirulina* species, *Chlorophyceae* (green algae) and 30 *Bacilliarophy* (diatom algae). Methyl glycidyl ether may come from glycerol methyl ethers which are impurities of a glycerol obtained by transesterification of fats or oils of animal or vegetable origin, as described in Patent Applications FR 06/05325 and FR 07/53863 filed in the name of Solvay SA, the contents of which are incorporated herein by reference. The haloketones such as, for 35 example, chloroacetone may be generated in the dichloropropanol manufacturing

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process by chlorination of glycerol and/or during step a) of the process according to the invention.

Steps a) and b) of the process used to manufacture the product according to the invention may be carried out under conditions such as those described in

5 Applications FR 07/53375 and FR 07/55448 filed in the name of Solvay SA.

The liquid reaction medium from step a) may especially contain an organic solvent, such as trichloropropane for example.

The dichloropropanol used in step a) can be fed to step a) as an aqueous composition, as an organic composition or a mixture thereof.

10 The dichloropropanol content of the aqueous composition is usually higher than or equal to 1 g/kg, often higher than or equal to 10 g/kg, frequently higher than or equal to 50 g/kg and particularly higher than or equal to 90 g/kg. That content is generally lower than or equal to 500 g/kg, usually lower than or equal to 200 g/kg, often lower than or equal to 150 g/kg, frequently lower than or equal to 120 g/kg and particularly lower than or equal to 110 g/kg. A content of 15 100 g/kg is convenient.

The dichloropropanol content of the organic composition is usually higher than or equal to 500 g/kg, often higher than or equal to 750 g/kg, frequently higher than or equal to 800 g/kg and particularly higher than or equal to 850 g/kg. That content is usually lower than or equal to 999 g/kg, often lower than or equal to 950 g/kg, frequently lower than or equal to 900 g/kg and particularly lower than or equal to 880 g/kg. A content of 870 g/kg is convenient.

20 In a particular embodiment, the mixture of dichloropropanol used in step a) of the process according to the invention can contain at least one chloro alkoxy propanol, as described in USP 61/007,661 of SOLVAY SA. The content of chloro alkoxy propanol in the dichloropropanol is usually lower than or equal to 0.2 g/kg, generally lower than or equal to 0.1 g/kg, often lower than or equal to 0.06 g/kg and frequently lower than or equal to 0.04 g/kg. This content is usually higher than or equal to 0.001 g/kg.

25 30 The chloro alkoxy propanol is often a chloro methoxy propanol. The chloro methoxy propanol can be selected from 2-chloro-3-methoxy-1-propanol, 1-chloro-3-methoxy-2-propanol, 3-chloro-2-methoxy-1-propanol, and any mixture of at least two of them.

35 Steps a) to c) of the process for obtaining the product according to the invention may independently be carried out in continuous or batch mode. It is preferred to carry out steps a) to c) in continuous mode.

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In the process according to the invention, the reaction from step a) may be carried out in one or more reaction zones, preferably in at least two reaction zones, more preferably in at least three reaction zones and more particularly preferably at least four reaction zones. The reaction zones may be composed of

- 5 volumes assembled in a single jacket or volumes in separate jackets. In the case where the volumes are assembled in a single jacket, the reaction zones may be positioned horizontally or vertically with respect to one another. In the case where the zones are positioned horizontally with respect to one another, the transfer from one zone to another may take place by gravity or by forced circulation. In the case of circulation by gravity, the transfer may be carried out with or without settling in one or in several channels. Transfer in a single channel without settling is preferred. In the case where the zones are assembled vertically, the transfer from one zone to another may take place by gravity or by forced circulation. Transfer by gravity is preferred. The implementation of step  
10 a) in a mechanically stirred column that is subdivided by perforated dividing plates is particularly preferred. The stirring may be carried out by any known means, for example by rotation of a spindle in the liquid medium or by pulsing of the flow. Columns stirred by rotation of a spindle are particularly preferred.  
15 These reaction zones may be placed in any configuration, in series, in parallel or some in series and others in parallel.

In the process according to the invention, the reaction zones may be supplied independently of one another with dichloropropanol, with the basic compound, with water or with at least two of these compounds. When several reaction zones are in series, it is preferred to supply the major part of the basic compound to the first reaction zone of the series.

The expression "reaction zones" is understood to mean zones where all the compounds needed for the reaction from step a) are found, namely dichloropropanol, the basic compound and an optional reaction solvent.

In the process for manufacturing the epichlorohydrin-based product  
30 according to the invention, the dichloropropanol may be dichloropropanol extrinsic to the process according to the invention, recycled dichloropropanol or a mixture of the two, such as has been defined before in Applications FR 07/53375 and FR 07/55448 filed in the name of Solvay SA. The expression "recycled dichloropropanol" is understood to mean dichloropropanol which has  
35 been separated in a step subsequent to step b) in the process according to the invention and which has then been recycled to step a) of said process. The term

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"extrinsic dichloropropanol" is understood to mean dichloropropanol which has not been recycled in the process according to the invention.

The temperature, pressure, reaction time and residence time may have different values in the various reaction zones, such as defined in Applications

5 FR 07/53375 and FR 07/55448 filed in the name of Solvay SA.

The ratio of the 2,3-dichloro-1-propanol content to the 1,3-dichloro-2-propanol content in the dichloropropanol may be different depending on the reaction zone to which the dichloropropanol is supplied. This ratio may be such as described in Applications FR 07/53375 and FR 07/55448 filed in the name of

10 Solvay SA.

The molar ratio of dichloropropanol to the basic compound may be different depending on the reaction zone to which these compounds are supplied. This ratio may be such as described in Applications FR 07/53375 and FR 07/55448 filed in the name of Solvay SA.

15 The basic compound may be an organic or inorganic basic compound.

Organic basic compounds are for example amines, phosphines and ammonium, phosphonium or arsonium hydroxides. Inorganic basic compounds are preferred. The expression "inorganic compounds" is understood to mean compounds which do not contain a carbon-hydrogen bond. The inorganic basic compound may be

20 chosen from alkali and alkaline-earth metal oxides, hydroxides, carbonates, hydrogencarbonates, phosphates, hydrogenphosphates and borates, and mixtures thereof. Alkali and alkaline-earth metal oxides and hydroxides are preferred.

Different basic compounds may be used in the various reaction zones where the reaction of step a) is carried out.

25 Generally, the temperature, reaction time or residence time and the molar ratio of dichloropropanol to the basic compound are higher in the reaction zones where the 2,3-dichloro-1-propanol/1,3-dichloro-2-propanol ratio is higher.

Step a) may be followed by an operation for neutralizing the excess basic compound.

30 It is possible to combine step a) or part of step a) with step b) in a common device compartmentalized into various reaction and settling zones.

The first fraction separated in step b) may have a composition such as that described for the first fraction separated in step b) of the epichlorohydrin manufacturing process which is the subject of Patent Applications FR 07/53375

35 and 075/55448 in the name of Solvay SA, of which the content is incorporated here by reference.

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The first fraction separated in step b) may contain, besides epichlorohydrin and trichloropropane, other organic compounds such as, for example, halogenated hydrocarbons other than trichloropropane, chloroacetone and methyl glycidyl ether, glycerol, hydroxyacetone, glycidol, acetaldehyde, acrolein, 5 acetone, ethylene oxide, propylene oxide and 2-butanone. These compounds may come from the dichloropropanol manufacturing process and/or be formed during the reaction between dichloropropanol and the basic compound during step a) of the process according to the invention.

10 The first fraction separated in step b) generally contains at least 100 g of epichlorohydrin/kg of first fraction, preferably at least 200 g/kg, even more preferably at least 300 g/kg, still more preferably at least 400 g/kg, more particularly preferably at least 500 g/kg, even more particularly preferably at least 600 g/kg, still more particularly preferably at least 700 g/kg, most particularly preferably at least 800 g/kg and very most particularly preferably at 15 least 850 g/kg. The epichlorohydrin content of the first fraction separated is generally at most 900 g/kg. The epichlorohydrin content of the first fraction separated depends, for example, on the use of an organic solvent and/or on an incomplete conversion of the mixture of 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol.

20 The first fraction separated in step b) generally contains at most 2 g of chloroacetone/kg of first fraction and usually at most 0.3 g/kg, commonly at most 0.1 g/kg, and particularly preferably at most 0.05 g/kg. The chloroacetone content is generally at least 0.005 g/kg.

25 The first fraction separated in step b) generally contains at most 5 g of acrolein/kg of first fraction, usually at most 0.3 g/kg and commonly at most 0.1 g/kg. The acrolein content is generally at least 0.07 g/kg.

30 The first fraction separated in step b) generally contains at most 20 g of chloroethers/kg of first fraction, usually at most 5 g/kg, commonly at most 2 g/kg, and particularly preferably at most 1 g/kg. The content of chloroethers is generally at least 0.5 g/kg.

35 Chloroethers are compounds of which the molecule comprises at least one chlorine atom and at least one oxygen atom, this oxygen atom being bonded to two carbon atoms. Epichlorohydrin is not considered here as a chloroether. These chloroethers preferably contain six carbon atoms. These chloroethers preferably contain two, sometimes three, chlorine atoms. These chloroethers preferably contain two oxygen atoms. These chloroethers are preferably chosen

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from compounds of crude chemical formula:  $C_6H_{10}Cl_2O_2$ ,  $C_6H_{12}Cl_2O$ ,  $C_6H_9Cl_1O_2$ ,  $C_6H_{11}Cl_1O_2$ , and mixtures of at least two of them.

The first fraction separated in step b) contains generally at most 10 g of chloroether of crude formula  $C_6H_{10}Cl_2O_2/kg$  of first fraction, usually at most 5 g/kg, commonly at most 0.5 g/kg, and particularly preferably at most 0.1 g/kg. The content of this chloroether is generally at least 0.05 g/kg.

The first fraction separated in step b) contains generally at most 5 g of chloroether of crude formula  $C_6H_{12}Cl_2O/kg$  of first fraction, usually at most 2 g/kg, commonly at most 0.5 g/kg, and particularly preferably at most 0.1 g/kg.

10 The content of this chloroether is generally at least 0.05 g/kg.

The first fraction separated in step b) contains generally at most 5 g of chloroether of crude formula  $C_6H_9Cl_1O_2/kg$  of first fraction, usually at most 2 g/kg, commonly at most 0.5 g/kg, and particularly preferably at most 0.1 g/kg. The content of this chloroether is generally at least 0.02 g/kg.

15 The first fraction separated in step b) contains generally at most 5 g of chloroether of crude formula  $C_6H_{11}Cl_1O_2/kg$  of first fraction, usually at most 2 g/kg, commonly at most 1 g/kg, and particularly preferably at most 0.6 g/kg. The content of this chloroether is generally at least 0.5 g/kg.

The first fraction separated in step b) generally contains other organic 20 compounds such as, for example, 1,3-dichloro-2-propanol, 2,3-dichloro-1-propanol and mixtures thereof. The sum of the contents of these dichloropropanols is generally less than or equal to 900 g/kg of first fraction, usually less than or equal to 800 g/kg, commonly less than or equal to 700 g/kg, in many cases less than or equal to 500 g/kg, often less than or equal to 300 g/kg 25 and frequently less than or equal to 200 g/kg. The sum of the contents of these dichloropropanols is generally at least 90 g/kg.

The first fraction separated in step b) generally contains other organic 30 compounds in addition to the epichlorohydrin, chloroacetone, acrolein, chloroethers and dichloropropanols.

The latter may come from the dichloropropanol manufacturing process and/or be formed during the reaction between dichloropropanol and the basic compound during step a) of the process according to the invention. Examples of these compounds are glycerol, 3-chloro-1,2-propanediol, 2-chloro-1,3-propanediol, and mixtures thereof, hydroxyacetone, glycidol, methyl glycidyl ether, 1,2,3-trichloropropane, cis- and trans-1,3-dichloropropenes, 1,3-dichloropropene and 2-chloro-2-propen-1-ol.

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The sum of the contents of glycerol, hydroxyacetone and glycidol is generally at most 100 g/kg of first fraction, usually at most 50 g/kg, commonly at most 30 g/kg, in particular at most 10 g/kg and specifically at most 1 g/kg. The sum of these contents is generally at least 0.1 g/kg.

5 The sum of the contents of 3-chloro-1,2-propanediol and 2-chloro-1,3-propanediol is generally at most 5 g/kg of first fraction, usually at most 3 g/kg, and commonly at most 1 g/kg. This sum is generally at least 0.5 g/kg.

10 The methyl glycidyl ether content is generally at most 5 g/kg of first fraction, usually at most 3 g/kg, and commonly at most 1 g/kg. This content is generally at least 0.005 g/kg.

15 The 1,2,3-trichloropropane content is generally at most 10 g/kg of first fraction, usually at most 5 g/kg, commonly at most 3 g/kg and particularly preferably at most 1 g/kg. This content is generally at least 0.0001 g/kg.

20 The sum of the contents of cis-and trans-1,3-dichloropropenes is generally at most 2 g/kg of first fraction, usually at most 1 g/kg, and commonly at most 0.1 g/kg. This sum is generally at least 0.01 g/kg.

25 The 1,3-dichloropropane content is generally at most 2 g/kg of first fraction, usually at most 1 g/kg, and commonly at most 0.5 g/kg. This content is generally at least 0.001 g/kg.

30 The 2-chloro-2-propen-1-ol content is generally at most 2 g/kg of first fraction, usually at most 1 g/kg, and commonly at most 0.5 g/kg. This content is generally at least 0.01 g/kg.

The first fraction separated in step b) generally contains water and inorganic compounds such as the basic compound and the salt.

35 The water content is generally at most 90 g/kg of first fraction, usually at most 80 g/kg, commonly at most 50 g/kg, often at most 30 g/kg and frequently at most 15 g/kg. The water content is generally at least 1 g/kg of first fraction.

The salt content is generally at most 10 g/kg of first fraction, commonly at most 5 g/kg, usually at most 2 g/kg, often at most 0.1 g/kg and frequently at most 0.015 g/kg. This salt content is generally at least 0.01 g/kg.

The proportion of salt present in the part of the liquid reaction medium from step a) before the settling step b) which is found in the first fraction separated in step b) is generally at most 25%, preferably at most 10% and more preferably at most 5%.

40 The salts are preferably chosen from alkali or alkaline-earth metal chlorides, sulphates, hydrogensulphates, hydroxides, carbonates,

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hydrogencarbonates, phosphates, hydrogenphosphates and borates, and mixtures thereof. Alkali and alkaline-earth metal chlorides are preferred. Calcium chloride and sodium chloride are more preferred. Sodium chloride is the most preferred salt.

- 5        The first fraction separated in step b) may also contain an acid compound. The acid compound may be chosen from monobasic and polybasic, organic and inorganic acids and mixtures thereof. Polybasic acids may be found in variously protonated forms. Inorganic acids are preferred. The expression "inorganic acid" is understood to mean acids of which the molecule does not contain a carbon-hydrogen bond, such as hydrogen chloride, carbonic acid and its acid salts, sulphuric acid and its acid salts, phosphoric acid and its acid salts and boric acid and its acid salts. Hydrogen chloride is preferred. This acid may be added to the part of the reaction medium from step a) as described in Application FR 07/53375 filed in the name Solvay SA.
- 10      The second fraction separated in step b) may have a composition such as that described for the second fraction separated in step b) of the epichlorohydrin manufacturing process which is the subject of Patent Applications FR 07/53375 and 07/55448 in the name of Solvay SA, of which the content is incorporated here by reference.
- 15      Among the supplementary treatments from step c), the liquid/liquid extraction, adsorption and distillation operations, alone or in combination, are preferred and the liquid/liquid extraction and distillation operations, alone or in combination, are particularly preferred.
- 20      In a first embodiment of step c) of the process for manufacturing the product according to the invention, the treatment from step c) comprises at least one liquid/liquid extraction operation for the first fraction separated in step b).
- 25      The extraction operation may be carried out cocurrently or countercurrently.
- 30      The cocurrent operation is generally carried out in at least one stirred reactor, followed by a settling tank. The countercurrent operation is generally carried out in at least one extraction column. Various type of reactors, settling tanks and extraction columns may be used, such as those described in "Perry's Chemical Engineers' Handbook", Sixth Edition, section 21, pp. 21, 55 and following".
- 35      The extraction solvent may be an organic composition or an aqueous composition.

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The extraction solvent is often an aqueous composition. Besides water, the aqueous composition may contain other compounds such as salts and/or basic compounds and/or acid compounds such as defined above and/or dichloropropanol. Frequently, the aqueous composition is essentially composed of water, particularly demineralised water.

5 After the extraction, a first part containing most of the epichlorohydrin which was contained in the first fraction before the extraction operation, and a second part containing most of the extraction solvent, are separated.

10 The proportion of epichlorohydrin present in the first fraction separated at the end of the settling step b) of the process according to the invention before the liquid/liquid extraction operation from step c), and which is found in the first part separated in step c), is preferably at least 80%, more preferably at least 90% and even more preferably at least 95%. These proportions are more particularly obtained when the extraction solvent is an aqueous composition.

15 The epichlorohydrin content of the first part separated in step c) is generally greater than 900 g of epichlorohydrin per kg of first part, preferably greater than or equal to 950 g/kg, more preferably greater than or equal to 990 g/kg and most particularly preferably greater than or equal to 999 g/kg. These contents are more particularly obtained when the extraction solvent is an aqueous composition.

20 The water content of the first part is generally less than or equal to 150 g of water per kg of first part, usually less than or equal to 100 g/kg, commonly less than or equal to 10 g/kg and particularly less than 1 g/kg.

25 These contents are more particularly obtained when the extraction solvent is an aqueous composition.

The content of organic extraction solvent from the first part separated in step c) is generally less than or equal to 100 g per kg of first part, usually less than or equal to 50 g/kg and particularly less than or equal to 1 g/kg.

30 The first part obtained at the end of the liquid/liquid extraction treatment from step c) may constitute the product according to the invention, in particular when the extraction solvent is water. This first part preferably constitutes the product according to the invention.

The first part separated in step c) may be subjected to subsequent treatments such as, for example, distillation, evaporation or stripping operations.

35 The second part separated in step c) generally contains the basic compound used in step a) of the process and/or the acid compound added before the settling

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step b) and/or the salt used and/or formed in step a) of the process, in particular when the extraction solvent is an aqueous composition.

The proportion of basic compound present in the first fraction separated at the end of the settling step b) of the process according to the invention before the liquid/liquid extraction operation from step c), and which is found in the second part separated in step c), is generally at least 80%, preferably at least 90% and more preferably at least 95%.

The proportion of salt present in the first fraction separated at the end of the settling step b) of the process according to the invention before the liquid/liquid extraction operation from step c), and which is found in the second part separated in step c), is generally at least 80%, preferably at least 90% and more preferably at least 95%.

These proportions are more particularly obtained when the extraction solvent is an aqueous composition.

The second part separated in step c) may be partially or completely recycled to step a), and/or after step a) and before step b) of the process. That second part is often recycled after step a) and before step b), frequently in the operation for neutralizing the excess basic compound after step a).

The second part separated in step c) may be subjected to a stripping, evaporation or distillation operation that makes it possible to recover the epichlorohydrin dissolved in this part.

In a second embodiment of step c) of the process for manufacturing the product according to the invention, in step c) the first fraction separated in step b) is subjected to a treatment which comprises at least one distillation operation, preferably at least two distillation operations and more preferably at least two distillation operations of which at least one is an operation for drying by azeotropic distillation. This treatment preferably comprises at least two distillation operations and more preferably at least four distillation operations and most particularly preferably at least six distillation operations in addition to the azeotropic distillation drying operation.

The expression "distillation operation" is understood to mean the separation of a mixture into two fractions of different compositions by a series of evaporation and condensation operations interconnected countercurrently and carried out in a specific device or in one part of a specific device. In the case where the separation of a mixture into N fractions of different compositions is

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carried out in a single physical jacket, it is considered that this corresponds to N-1 distillations.

The operation for drying by azeotropic, preferably heteroazeotropic, distillation with removal of an aqueous phase and of an organic phase, preferably with removal of an aqueous phase, may be carried out before the other distillation operations. The azeotropic distillation drying operation may be carried out after one or more of the other distillation operations.

In this second embodiment, after the treatment from step c), two portions are obtained.

10 In this second embodiment, the proportion of epichlorohydrin present in the first fraction separated at the end of the settling step b) of the process according to the invention before the treatment from step c), and which is found in the first portion separated in step c), is generally at least 80%, preferably at least 90% and more preferably at least 95%.

15 In this second embodiment, the proportion of dichloropropanol present in the first fraction separated at the end of the settling step b) of the process according to the invention before the treatment from step c), and which is found in the second portion separated in step c), is generally at least 80%, preferably at least 90% and more preferably at least 95%.

20 In this second embodiment, the first portion obtained at the end of the distillation operations of the treatment from step c) may constitute the product according to the invention. This first portion preferably constitutes the product according to the invention.

25 In this second embodiment, the second portion may be partially or completely recycled to step a) of the process to obtain the product according to the invention.

30 In a third embodiment of step c) of the process for manufacturing the product according to the invention, in step c) the first fraction separated in step b) is subjected to a treatment which comprises at least one adsorption operation and at least one distillation operation, and preferably at least three distillation operations and more preferably at least five distillation operations.

35 The expression "distillation operation" is understood to mean the separation of a mixture into two fractions having different compositions by a series of evaporation and condensation operations interconnected countercurrently and carried out in a specific device or in one part of a specific device. In the case where the separation of a mixture into N fractions of different

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compositions is carried out in a single physical jacket, it is considered that this corresponds to N-1 distillations.

In this third embodiment, the adsorption operation may be carried out before the distillation operations. The adsorption operation may be carried out 5 after one or more distillation operations. The object of the adsorption operation is generally to reduce the water content of the fractions treated. The adsorbants generally used are adsorbants such as molecular sieves 3A, 4A and 5A.

In this third embodiment, after the treatment from step c), two cuts are obtained.

10 In this third embodiment, the proportion of epichlorohydrin present in the first fraction separated at the end of the settling step b) of the process according to the invention before the treatment from step c), and which is found in the first cut separated in step c), is generally at least 80%, preferably at least 90% and more preferably at least 95%.

15 In this third embodiment, the proportion of dichloropropanol present in the first fraction separated at the end of the settling step b) of the process according to the invention before the treatment from step c), and which is found in the second cut separated in step c), is generally at least 80%, preferably at least 90% and more preferably at least 95%.

20 In this third embodiment, separated at the end of the treatments described in the second and third embodiments is epichlorohydrin, of which the water content is generally less than 0.5 g of water per kg of epichlorohydrin, usually less than or equal to 0.1 g/kg and commonly less than or equal to 0.05 g/kg. In this epichlorohydrin, the content of organic compounds having a boiling point 25 under a pressure of 1 bar absolute less than or equal to the boiling point of epichlorohydrin is generally less than or equal to 0.3 g of these compounds per kg of epichlorohydrin, usually less than or equal to 0.2 g/kg and commonly less than or equal to 0.1 g/kg. These compounds are, for example, acrolein, methyl glycidyl ether and chlororacetone. In this epichlorohydrin, the content of organic 30 compounds having a boiling point under a pressure of 1 bar absolute greater than or equal to the boiling point of epichlorohydrin is generally less than or equal to 0.7 g of these compounds per kg of epichlorohydrin, usually less than or equal to 0.5 g/kg and commonly less than or equal to 0.3 g/kg. These compounds are, for example, 2-chloro-2-propen-1-ol, dichloropropene, dichloropropane, 35 hydroxyacetone, trichloropropane, glycidol, dichloropropanol, monochloropropanediol, glycerol and chloroethers such as mentioned above.

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In this third embodiment, the first cut obtained at the end of the treatment from step c) may constitute the product according to the invention. This first portion preferably constitutes the product according to the invention

5 In a fourth embodiment of step c) of the process for manufacturing the product according to the invention, which is preferred, the first and second embodiments are combined and in one preferred variant, initially, the first fraction separated in step b) is subjected to at least one liquid/liquid extraction operation with an aqueous composition and in which a first part containing most of the epichlorohydrin which was contained in the first fraction before the  
10 extraction operation is separated, and this first part is subjected to at least one treatment which comprises at least one operation for drying by azeotropic distillation and at least one distillation operation.

In this fourth embodiment, after the treatment from step c), two cuts are obtained.

15 In this fourth embodiment, the proportion of epichlorohydrin present in the first fraction separated at the end of the settling step b) of the process according to the invention before the treatment from step c), and which is found in the first cut separated in step c), is generally at least 80%, preferably at least 90% and more preferably at least 95%.

20 In this fourth embodiment, the proportion of dichloropropanol present in the first fraction separated at the end of the settling step b) of the process according to the invention before the treatment from step c), and which is found in the second cut separated in step c), is generally at least 80%, preferably at least 90% and more preferably at least 95%.

25 In this fourth embodiment, separated at the end of the treatment from step c) is epichlorohydrin, of which the water content is generally less than 0.5 g of water per kg of epichlorohydrin, usually less than or equal to 0.1 g/kg and commonly less than or equal to 0.05 g/kg. In this epichlorohydrin, the content of organic compounds having a boiling point under a pressure of 1 bar absolute less than or equal to the boiling point of epichlorohydrin is generally less than or equal to 0.3 g of these compounds per kg of epichlorohydrin, usually less than or equal to 0.2 g/kg and commonly less than or equal to 0.1 g/kg. In this epichlorohydrin, the content of organic compounds having a boiling point under a pressure of 1 bar absolute greater than or equal to the boiling point of epichlorohydrin is generally less than or equal to 0.7 g of these compounds per

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kg of epichlorohydrin, usually less than or equal to 0.5 g/kg and commonly less than or equal to 0.3 g/kg.

In this fourth embodiment, the first cut obtained at the end of the treatment from step c) may constitute the product according to the invention. This first cut preferably constitutes the product according to the invention.

Brief description of the Figures

Figure 1 : first scheme of an installation used for obtaining the product according to the invention

Figure 2 : second scheme of an installation used for obtaining the product according to the invention

Figure 3 : third scheme of an installation used for obtaining the product according to the invention

Figure 4 : examples of chemical formula of epoxy resins

Figure 5 : examples of chemical formula of compounds having at least one aromatic hydroxyl group

Figure 6 : examples of chemical formula of compounds having at least one aromatic hydroxyl or aromatic amine group per molecule

Figure 7 : examples of chemical formula of polycyclopentadiene polyphenols or aromatic polyamines

Figure 8 : example of chemical formula of a coagulant molecule

Figure 9 : example of chemical formula of wet-strength resin polymers

Figure 10 : example of chemical formula of compounds used as phosphorus containing flame retardants.

Figure 1 shows a first scheme of an installation used for obtaining the product according to the invention.

In a first variant of this first scheme, a first reactor (1) is supplied with a first stream of dichloropropanol via the line (2) and a first stream of basic compound via the line (3). Drawn off from the reactor (1) via the line (4) is a stream comprising epichlorohydrin, salt, dichloropropanol and basic compound

which have not reacted, and a second reactor (5) is supplied with this stream.

The reactor (5) is supplied with a second stream of dichloropropanol via the line (6) and with a second stream of basic compound via the line (7). Drawn off from the second reactor (5) via the line (8) is a stream comprising epichlorohydrin and salt, and a first settling tank (9) is supplied with this stream.

In the first settling tank (9), a first fraction containing most of the epichlorohydrin contained in the stream (8) and a second fraction containing

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most of the salt which was contained in the stream (8) are separated. The second fraction is drawn off from the settling tank (9) via the line (10) and the first fraction via the line (11). A first part of the first fraction drawn off from the line (11) supplies a first extractor (13) via the line (12). The first extractor (13) is  
5 also supplied with water via the line (14). Vigorous stirring is carried out in the first extractor (13). A stream is drawn off from the extractor (13) via the line (15) and a second settling tank (16) is supplied with this stream. Drawn off from the second settling tank (16) via the line (17) is a third fraction containing most  
10 of the epichlorohydrin contained in the stream (15) and a fourth fraction containing water and the salts via the line (18).

In various aspects of this first variant of this first scheme, a portion of the fourth fraction containing water and the salts, drawn off via the line (18), is respectively recycled to the first reactor (1) via the line (19) and/or between the first reactor (1) and the second reactor (5) via the line (20) and/or between the  
15 second reactor (5) and the first settling tank (9) via the line (21).

In a second variant of this first scheme, the procedure from the first variant is followed except that the first fraction drawn off from the first settling tank (9) via the line (11) no longer supplies the extractor (13) but supplies an extraction column (23) via the line (22). The extraction column (23) is supplied  
20 countercurrently with water via the line (24). Drawn off from the column (23) is a fifth fraction containing most of the epichlorohydrin contained in the stream (22), via the line (25), and a sixth fraction containing water and the salts, via the line (26).

In various aspects of this second variant of this first scheme, a portion of  
25 the second fraction containing water and the salts, drawn off via the line (26), is respectively recycled to the first reactor (1) via the line (27) and/or to the second reactor (5) via the line (28) and/or between the second reactor (5) and the first settling tank (9) via the line (29).

In third and fourth variants of this first scheme, the procedure from the first  
30 variant or from the second variant respectively is followed, and in addition, a third reactor (30) is supplied with a third stream of dichloropropanol via the line (31) and a third stream of basic compound via the line (32). Drawn off from the reactor (30) via the line (33) is a stream comprising epichlorohydrin, salt,  
35 dichloropropanol and basic compound which have not reacted, and a fourth reactor (34) is supplied with this stream. The fourth reactor (34) is supplied with a fourth stream of dichloropropanol via the line (35) and with a fourth stream of

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basic compound via the line (36). Drawn off from the fourth reactor (34) via the line (37) is a stream comprising epichlorohydrin and salt, and the first settling tank (9) is supplied with this stream.

In various aspects of these third and fourth variants of this embodiment,  
5 the third reactor (30) is supplied with steam via the line (38) and drawn off from the third reactor (30), via the line (39), is a stream containing water and epichlorohydrin, and/or the fourth reactor (34) is supplied with steam via the line (40) and drawn off from the fourth reactor (34), via the line (41), is a stream containing water and epichlorohydrin.

10 In these various variants, part of the streams (18) and/or (26) may supply a purge via the lines (42) and (43) respectively.

Without being bound by any theory, one believes that in the a mixture of dichloropropanol containing 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol, the 1,3-dichloro-2-propanol isomer is mainly converted into epichlorohydrin in the first reactors (1) and/or (30), while the 2,3-dichloro-1-propanol isomer is mainly converted into epichlorohydrin in the second reactors (5) and/or (34).

Figure 2 shows a second scheme of an installation used for obtaining the product according to the invention.

20 In a first variant of this second scheme, an azeotropic drying column (50) is supplied with a stream containing epichlorohydrin via the line (51). This stream comes from one or more lines of the installation described in Figure 1, i.e. the lines (17), (25) and also the organic fraction of the lines (39) and (41). This stream contains, besides epichlorohydrin, light products, that is to say of which  
25 the boiling point under a pressure of 1 bar absolute is below the boiling point of epichlorohydrin, such as acetaldehyde and acrolein, water, heavy products, that is to say of which the boiling point under a pressure of 1 bar absolute is above the boiling point of epichlorohydrin and below the boiling point of dichloropropanol, such as glycidol, 2-chloro-2-propen-1-ol, hydroxyacetone,  
30 chloroacetone, 1,3-dichloropropene, 1,3-dichloropropene, 1,2,3-trichloropropene, 2-methyl-2-cyclopenten-1-one, cyclopentanone, 2-chloroethanol and chloropropanol, and super-heavy products, that is to say of which the boiling point under a pressure of 1 bar absolute is above the boiling point of dichloropropanol, such as monochloropropanediol and partially  
35 chlorinated and/or esterified glycerol oligomers.

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Drawn off from the column (50) via the line (52) is a stream containing water, epichlorohydrin, light products and heavy products that form an azeotrope with water, and a first condenser (53), then a first settling tank (55), are supplied with this stream via the line (54). Drawn off from the first settling tank (55) is a  
5 water phase, via the line (56), and epichlorohydrin saturated with water, via the line (57). The water phase can be further sent to a High Temperature Oxidation treatment Unit. A first part of the stream drawn off via the line (57) optionally supplies the distillation column (50) via the line (58). A second part of the stream drawn off via the line (57) supplies a second distillation column (60) via  
10 the line (59). Drawn off from the second column (60) via the line (61) is a stream which essentially contains light products and a second condenser (96), then a second settling tank (97), are supplied with this stream via the line (61). Drawn off from the second settling tank (97) is a gas phase containing light products, via the line (99) which can be further sent to a High Temperature  
15 Oxidation treatment Unit. Drawn off from the second settling tank (97) is a water phase, via the line (98) which can be further sent to a High Temperature Oxidation treatment Unit. A part of the liquid contained in the settling tank (97), preferably of the organic phase, can be returned to the top of the distillation column (60) via the line (106). Drawn off from the second distillation column  
20 (60) via the line (62) is a stream containing mainly epichlorohydrin, and the first distillation column (50) is supplied with this stream.

Drawn off from the column (50) via the line (63) is a stream scrubbed of water, and a third distillation column (64) is supplied with this stream.

Drawn off from the third column (64) via the line (65) is a stream  
25 containing epichlorohydrin, light products and heavy products. This stream supplies a fourth distillation column (66) drawn off from which, via the line (67), is a stream that essentially contains light products. One part of this stream may be returned to the first distillation column (50) via the line (68). Drawn off from the fourth distillation column (66) via the line (69) is a stream depleted of light  
30 compounds, and a fifth distillation column (70) is supplied with this stream. Drawn off from the fifth distillation column (70) via the line (71) is purified epichlorohydrin and via the line (72) a stream comprising heavy products of which one part may be conveyed to the third distillation column (64) via the line (73).

35 Drawn off from the third column (64) via the line (74) is a stream comprising epichlorohydrin, heavy products, dichloropropanol and super-heavy

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products, and a sixth distillation column (75) is supplied with this stream.

Drawn off from the sixth distillation column (75) via the line (76) is a stream containing epichlorohydrin and heavy products, and a twelfth distillation column (100) is supplied with this stream and drawn off from the sixth distillation

5 column (75) via the line (77) is a stream containing dichloropropanol and super-heavy products, and a seventh distillation column (78) is supplied with this stream.

Drawn off from the twelfth distillation column (100) via the line (102) is a stream containing epichlorohydrin and that stream is recycled back to the first

10 distillation column (50). Drawn off from the twelfth distillation column (100) via the line (101) is a stream containing heavy products and that stream can be further treated in a High Oxidation Temperature Unit.

Drawn off from the seventh distillation column (78) via the line (79) is a stream of dichloropropanol, and via the line (80) a stream containing super-

15 heavy products. The stream of dichloropropanol collected via the line (79) may be conveyed to one or more of the reactors (1), (5), (30) and (34) of the installation described in Figure 1. The stream containing super-heavy products can be sent for further treatment a High Temperature Oxidation Unit.

In a second variant of the second scheme, the procedure from the first

20 variant is followed except that the lines and columns (74) to (80) are absent and drawn off from the third column (64) via the line (81) is a stream comprising epichlorohydrin, heavy products, dichloropropanol and super-heavy products, and an eighth distillation column (82) is supplied with this stream. Drawn off from the eighth distillation column (82) via the line (83) is a stream containing 25 super-heavy products, which can be further treated in a High Temperature Oxidation Unit and via the line (84) a stream containing epichlorohydrin, heavy products and dichloropropanol, and a ninth distillation column (85) is supplied with this stream.

30 Drawn off from the ninth distillation column (85) via the line (86) is a stream of dichloropropanol, and via the line (87) a stream containing epichlorohydrin and heavy products, and the twelfth distillation column 100 is supplied with this stream. The stream of dichloropropanol collected via the line (86) may be conveyed to one or more of the reactors (1), (5), (30) and (34) of the installation described in Figure 1.

35 In a third variant of this second scheme, the procedure from the first variant is followed except that the lines and columns (65) to (73) are absent.

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Drawn off from the third column (64) via the line (88) is a stream containing epichlorohydrin, light products and heavy products. This stream supplies a tenth distillation column (89) drawn off from which, via the line (90), is a stream that contains heavy products. One part of this stream may be returned 5 to the third distillation column (64) via the line (91). Drawn off from the tenth distillation column (89) via the line (92) is a stream containing epichlorohydrin and light products, and an eleventh distillation column (93) is supplied with this stream. Drawn off from the eleventh distillation column (93) via the line (94) is 10 a stream of purified epichlorohydrin, and via the line (95) a stream containing light compounds. One part of this stream may be conveyed to the first distillation column (50) via the line (96).

In a fourth variant of this second scheme, the procedure from the second variant is followed except that the lines and columns (65) to (73) are absent.

Drawn off from the third column (64) via the line (88) is a stream 15 containing epichlorohydrin, light products and heavy products. This stream supplies a tenth distillation column (89) drawn off from which, via the line (90), is a stream that contains heavy products. One part of this stream may be returned to the third distillation column (64) via the line (91). Drawn off from the tenth distillation column (89) via the line (92) is a stream containing epichlorohydrin 20 and light products, and an eleventh distillation column (93) is supplied with this stream. Drawn off from the eleventh distillation column (93) via the line (94) is a stream of purified epichlorohydrin, and via the line (95) a stream containing light compounds. One part of this stream may be conveyed to the first distillation column (50) via the line (96).

25 In a fifth variant of this second scheme, the procedure from the first variant is followed except that the lines and columns (69) to (73) are absent.

Drawn off from the third column (66) via the line (103) is a stream containing epichlorohydrin, via line (104) a stream containing heavy products a part of which can be recycled to the third distillation column (64) via line (105).

30 Figure 3 shows a third scheme of an installation used for obtaining the product according to the invention.

In a first variant of this third scheme, a first distillation column (200) is supplied with a stream containing epichlorohydrin via the line (201). This stream comes from one or more lines of the installation described in Figure 1, 35 i.e. the lines (17) and (25), and the organic fraction of lines (39) and (41). This stream contains, besides epichlorohydrin, light products, that is to say of which

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the boiling point under a pressure of 1 bar absolute is below the boiling point of epichlorohydrin, such as acetaldehyde and acrolein, water, heavy products, that is to say of which the boiling point under a pressure of 1 bar absolute is above the boiling point of epichlorohydrin and below the boiling point of

- 5 dichloropropanol, such as glycidol, 2-chloro-2-propen-1-ol, hydroxyacetone, chloroacetone, 1,3-dichloropropane, 1,3-dichloropropene, 1,2,3-trichloropropane, 2-methyl-2-cyclopenten-1-one, cyclopentanone, 2-chloroethanol and chloropropanol, dichloropropanol and super-heavy products, that is to say of which the boiling point under a pressure of 1 bar absolute is  
10 above the boiling point of dichloropropanol, such as monochloropropanediol and partially chlorinated and/or esterified glycerol oligomers.

Drawn off from the distillation column (200) via the line (202) is a stream containing epichlorohydrin, water, light compounds and heavy compounds, and an azeotropic drying column (203) is supplied with this stream. Drawn off from  
15 the drying column (203) via the line (204) is a stream containing epichlorohydrin and water that is conveyed to a settling tank (207) via a condenser (205) and via the line (206). Drawn off from the settling tank (207) via the line (208) is a stream mostly containing water and, via the line (209) a stream mostly containing epichlorohydrin that is conveyed to the distillation column (200).

- 20 Drawn off from the azeotropic drying column (203) via the line (210) is a stream containing epichlorohydrin, light compounds and heavy compounds, and a second distillation column (211) is supplied with this stream. Drawn off from the second distillation column (211) via the line (212) is a stream containing light compounds, and via the line (213) a stream containing epichlorohydrin and  
25 heavy compounds, and a third distillation column (214) is supplied with this stream. Drawn off from the column (214) via the line (215) is a stream composed of purified epichlorohydrin, and via the line (216) a stream containing heavy compounds that are recycled to the first distillation column (200).

- 30 Drawn off from the first distillation column (200) via the line (217) is a stream containing dichloropropanol, heavy compounds and super-heavy compounds, and a fifth distillation column (218) is supplied with this stream. Drawn off from the column (218) via the line (219) is a stream containing super-heavy products, and via the line (220) a stream containing dichloropropanol and heavy products, and a sixth distillation column (221) is supplied with this stream.  
35 Drawn off from the column (221) via the line (222) is a stream mostly containing

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dichloropropanol, and via the line (223) a stream essentially containing heavy products.

The stream of dichloropropanol collected via the line (222) may be conveyed to one or more of the reactors (1), (5), (30) and (34) of the installation  
5 described in Figure 1.

In a second variant of the third scheme, the procedure from the first variant is followed except that the lines and columns (217) to (223) are absent and drawn off from the first column (200) via the line (224) is a stream comprising heavy products, dichloropropanol and super-heavy products, and a seventh distillation column (225) is supplied with this stream. Drawn off from the seventh distillation column (225) via the line (226) is a stream containing heavy products, and via the line (227) a stream containing super-heavy products and dichloropropanol, and an eighth distillation column (228) is supplied with this stream.  
10

15 Drawn off from the eighth distillation column (228) via the line (229) is a stream of dichloropropanol, and via the line (230) a stream containing super-heavy products. The stream of dichloropropanol collected via the line (229) may be conveyed to one or more of the reactors (1), (5), (30) and (34) of the installation described in Figure 1.

20 In a third variant of the third scheme, the procedure from the first variant is followed except that the lines and columns (210) to (216) are absent.

25 Drawn off from the drying column (203) via the line (231) is a stream containing epichlorohydrin, light products and heavy products. This stream supplies a ninth distillation column (232) drawn off from which, via the line (233), is a stream that contains heavy products. Drawn off from the ninth distillation column (232) via the line (234) is a stream containing epichlorohydrin and light products, and a tenth distillation column (235) is supplied with this stream. Drawn off from the tenth distillation column (235) via the line (236) is a stream of purified epichlorohydrin, and via the line (237) a stream containing light compounds.  
30

35 In a fourth variant of the third scheme, the procedure from the second variant is followed except that the lines and columns (210) to (216) are absent.

Drawn off from the drying column (203) via the line (231) is a stream containing epichlorohydrin, light products and heavy products. This stream supplies an eighth distillation column (232) drawn off from which, via the line (233), is a stream that contains heavy products. Drawn off from the eighth

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distillation column (232) via the line (234) is a stream containing epichlorohydrin and light products, and a ninth distillation column (235) is supplied with this stream. Drawn off from the ninth distillation column (235) via the line (236) is a stream of purified epichlorohydrin, and via the line (237) a stream containing light compounds.

5 Other variants of the various embodiments can easily be envisaged.

The invention also relates to the use of the epichlorohydrin-based product described above as a reactant in a process for manufacturing epoxy resins, synthetic glycerol, polyamide-epichlorohydrin resins, chemical formulations for 10 water treatment, such as polyacrylamides, polyamines and quaternary ammonium salts, epichlorohydrin elastomers, such as epichlorohydrin homopolymers, epichlorohydrin/ethylene oxide copolymers and epichlorohydrin/ethylene oxide/allyl glycidyl ether terpolymers, glycidyl ethers, such as cresyl glycidyl, butyl, decyl or dodecyl ethers, surfactants, flame 15 retardants, such as phosphorylated flame retardants, resins for the production of water-resistant paper and glycidyl acrylates and methacrylates.

The presence of impurities in epichlorohydrin may prove troublesome in some of these applications for various reasons. Some halogenated hydrocarbons for instance are or are suspected to be carcinogenic, are suspected to have 20 development toxicity, reproductive toxicity, cardiologic toxicity, endocrine toxicity, immunotoxicity and toxicity to the liver, the kidneys, the nerves, the respiratory tract and to the skin. They can remain in the final products and possibly degrade with a concomitant deterioration of the properties of the final products. They can exhibit or degrade in compounds exhibiting some toxicity 25 leading to safety issues especially when the final products are intended to be in contact with food and drink. Moreover, they can accumulate in and contaminate industrial waters such as wastewaters for instance or water containing pulp that is recycled in the pulp and paper industry. In the latter case, their higher concentration can increase contamination of the paper made using the recycled 30 water.

A further goal of the invention is to solve those problems by providing a product containing epichlorohydrin and a reduced level of impurities which can be used in the manufacture of epoxy derivatives, of products which will be used in food and drink applications, of cationization agents, of flame retardants, of 35 products which will be used as detergent ingredients, and of epichlorohydrin elastomers.

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The invention is therefore also related to the use of the product according to the invention in the manufacture of epoxy resins or glycidyl esters or glycidyl ethers or glycidyl amides or glycidyl imides or coagulants or wet-strength resins or cationization agents or flame retardants or detergent ingredients or

5 epichlorohydrin elastomers.

### 1. EPOXY DERIVATIVES

#### 1.1. General

Epoxy derivatives are for example, epoxy resins, glycidyl ethers, glycidyl esters and glycidyl amides and imides. Examples of glycidyl esters are glycidyl 10 acrylate and glycidyl methacrylate.

By epoxy resin, one intend to denote a polymer, the chemical formula of which contains at least one oxirane group, preferably one 2,3-epoxypropoxy group.

By polymer, one intends to denote molecules with many units joined to each other through chemical covalent bonds, often in a repeating manner, those units being referred as repeat units. The number of repeat units is higher than zero. A polymer contains at least one type of repeat units. When the polymer contains only one type of repeat units, it is called a homopolymer. When the polymer contains more than one type of repeat units, it is called a copolymer.

20 The copolymers can be of the random type, of the alternating type or of the block type, such as described in "Polymer Science Dictionary, M.S.M., Elsevier Applied Science, London and New York 1989, page 86".

Examples of chemical formulas of epoxy resins are presented in Figure 4, where n is not zero.

25 By glycidyl ether, one intends to denote an ether, the chemical formula of which contains at least one glycidyl (2,3-epoxypropyl) group and which is not a polymer. Examples of glycidyl ethers are N-butyl glycidyl ether, C<sub>12</sub>-C<sub>14</sub> aliphatic glycidyl ethers, o-Cresol glycidyl ether, neopentylglycol diglycidyl ether and butanediol diglycidyl ether.

30 By glycidyl ester, one intends to denote an ester, the chemical formula of which contains at least one glycidyl (2,3-epoxypropyl) group and which is not a polymer. Examples of glycidyl ester are diglycidyl ester of hexahydrophthalic acid, glycidyl ester of neodecanoic acid, glycidyl acrylate and glycidyl methacrylate.

35 By glycidyl amides and imides, one intends to denote an amide or an imide, the chemical formula of which contains at least one glycidyl (2,3-

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epoxypropyl) group and which is not a polymer. Examples of glycidyl amide and imide 1,3,5—tris(2,3-epoxypropyl)-1,3,5-perhydrotriazine-2,4,6-trione and 5,5-dimethyl-1,3-bis(2,3-epoxypropyl)-2,4-imidazolidinedione.

#### 1.2. Co-reactants

- 5 When, the product containing epichlorohydrin according to the invention is used in the manufacture of epoxy derivatives, the product containing epichlorohydrin is usually subjected to a reaction with at least one compound containing at least one active hydrogen atom, preferably at least two active hydrogen atoms, followed by dehydrochlorination as described in Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, 1987, Vol. A9, pp. 547-553).
- 10 The compound containing one active hydrogen atom can be selected from mono alcohol, preferably from 1-butanol, a C<sub>12</sub> to C<sub>14</sub> primary alcohol or a cresol, and mixtures thereof, mono carboxylic acids, like for instance neodecanoic acid, acrylic acid, methacrylic acid, or mixtures thereof.
- 15 The compound containing at least two active hydrogen atoms can be selected from polyols, polyamines, amino alcohols, polyimides and amides, polycarboxylic acids, and mixtures thereof.
- 20 The polyols can be aromatic or aliphatic. Aromatic polyols are preferred. Preferred aliphatic polyols are aliphatic diols, more preferably selected from butanediol, neopentyl glycol, hydrogenated Bisphenol A (4,4'-dihydroxy-2,2-dicyclohexylpropane), and aliphatic triols, preferably glycerol, poly(oxypropylene) glycol, and mixtures thereof.
- 25 Aromatic polyols can be selected from polyhydroxy benzenes, polyphenolic compounds, and mixtures thereof.
- 30 Poly hydroxybenzenes are preferably selected from dihydroxy benzenes, trihydroxy benzene, and mixtures thereof. Dihydroxy benzenes are more preferably selected from 1,2-, 1,3-, 1,4-dihydroxy benzenes and mixture thereof. Trihydroxy benzene is preferably 1,3,5-trihydroxy benzene.
- 35 Polyphenolic compounds are generally compounds the molecule of which contains at least one aromatic hydroxyl group.
- Suitable compounds having at least one aromatic hydroxyl group which can be employed herein are such as described in US 4,499,255, the content of which is incorporated herein by reference and include, for example, phenols, bisphenols, novolac resins, polyvinyl phenols, the corresponding amine compounds and the like, such as those represented by the formulas I to V of

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Figure 5 wherein, each A is independently a divalent hydrocarbon group having from 1 to about 12, preferably from 1 to about 6 carbon atoms, -O-, -S-, -S-S-, -(S=O)<sub>2</sub>-, -(S=O)- or -(C=O)-, A' is a trivalent hydrocarbon group having from 1 to about 12, preferably from 1 to about 6, carbon atoms; each R is  
5 independently hydrogen, a hydrocarbyl group having from 1 to about 10, preferably from 1 to about 4, carbon atoms, a halogen atom, preferably chlorine or bromine or a hydroxyl group or an amino group; each Z is independently -OH or NH<sub>2</sub>; p has a value of from about 1 to about 100, preferably from about 2 to about 50; m has a value from about 1.00 to about 6 and n has a value of zero  
10 or 1.

Also suitable as compounds having at least one aromatic hydroxyl or aromatic amine group per molecule are those represented by the formulas VI to VIII of Figure 6, wherein each R is a divalent hydrocarbyl group having from 1 to about 18, preferably from about 2 to about 12 and most preferably from  
15 about 2 to about 6 carbon atoms, a group represented by the formulas IX, X, XI or XII of Figure 6, or R can combine with R<sup>1</sup> so as to form a stable heterocyclic ring with the nitrogen atoms; each A is independently a divalent hydrocarbyl group having from 1 to about 10, preferably from 1 to about four carbon atoms, -O-, -S-, -S-S-, -(S=O)<sub>2</sub>-, -(S=O)- or -(C=O)-, each R<sup>1</sup> is independently hydrogen, a 2,3-epoxypropyl group, a 2-alkyl-2,3-epoxypropyl group, a monovalent hydrocarbyl group or a hydroxyl substituted monovalent hydrocarbyl group, said hydrocarbyl groups having from 1 to about 9 carbon atoms, said alkyl having from 1 to about 4, preferably 1 to about 3 carbon atoms; each R<sup>2</sup> is independently hydrogen or an alkyl group having from 1 to about 4, preferably 1 to about 3  
20 carbon atoms; each R<sup>3</sup> is independently hydrogen or an alkyl group having from 1 to about 4 carbon atoms; each R<sup>4</sup> is independently hydrogen, a hydrocarbyl or halogen substituted hydrocarbyl group having from 1 to about 9, preferably from 1 to about 2 carbon atoms; each R<sup>8</sup> is independently selected from the group represented by formula XIV or the same groups as R<sup>1</sup> except that R<sup>8</sup> cannot be a  
25 hydrogen; each R<sup>9</sup> is independently a divalent hydrocarbyl group having from 2 to about 4, preferably 2 carbon atoms; each Z is independently -OH or -NH<sub>2</sub>; each X is independently hydrogen, chlorine, bromine or a hydrocarbyl or a hydrocarbyloxy group having from 1 to about 9, preferably 1 to about 6 carbon atoms; each m independently has a value of zero or 1; n has an average value of  
30 from about 0.01 to about 6, preferably 0.1 to about 4; p has an average value of from 1 to about 10, preferably from 1 to about 3; q has an average value of at  
35

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least 1, preferably from 1 to about 150, most preferably from 1 to about 100 and usually from 1 to about 10 and each y and z independently has a value of 1 or 2.

Also suitable are polycyclopentadiene polyphenols or aromatic polyamines represented by the formula XIII of Figure 7, wherein Z is -OH or -NH<sub>2</sub> and n has a value from 1 to about 5; n' has a value of from about 1 to about 10, preferably from 3 to about 6; each R is independently hydrogen, a hydrocarbyl group having from 1 to about 10, preferably from 1 to about 4 carbon atoms, a halogen atom, preferably chlorine or bromine or a hydroxyl group or an amino group.

Suitable such polycyclopentadiene polyphenols and methods for their preparation can be found in U.S. Pat. No. 4,390,680 issued to Donald L. Nelson on June 28, 1983 which is incorporated herein by reference. The polycyclopentadiene aromatic polyamines can be prepared in a similar manner by substituting an aromatic amine for the phenolic compound.

Also suitable are compounds containing both at least one aromatic hydroxyl group and at least one aromatic amine group such as, for example, hydroxy aniline, aminoxylenol and the like.

The polyphenolic compound is preferably selected from Bisphenol A (4,4'-dihydroxy-2,2-diphenylpropane, 4,4'-isopropylidenediphenol), tetrabromo Bisphenol A (4,4'-isopropylidenebis(2,6-dibromophenol)), Bisphenol AF (4,4'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bisphenol) = hexafluorobisphenol A (4,4'-dihydroxy-2,2-diphenyl-1,1,1,3,3,3-hexafluoropropane), 1,1,2,2-tetra(p-hydroxyphenyl)ethane, hexafluorobisphenol A, tetramethylbisphenol (4,4'-dihydroxy-3,3',5,5'-tetramethyl bisphenol), 1,5-dihydroxynaphthalene, 1,1',7,7'-tetrahydroxy-dinaphthyl methane, 4,4'-dihydroxy- $\alpha$ -methylstilbene, a condensation product of Bisphenol A with formaldehyde (Bisphenol A novolac), a condensation product of phenol with formaldehyde, preferably Bisphenol F (mixture of o,o', o,p' and p,p' isomers of dihydroxy diphenylmethane), a condensation product of cresol with formaldehyde (mixtures of o,o', o,p' and p,p' isomers of methyl hydroxy diphenylmethane), an alkylation product of phenol and dicyclopentadiene (2,5-bis[(hydroxy phenyl]octahydro-4,7-methano-5H-indene), a condensation product of phenol and glyoxal (tetrakis(4-hydroxyphenyl)ethane), a condensation product of phenol and a hydroxybenzaldehyde (e.g., tris(4-hydroxyphenyl)methane), 1,1,3-tris-(p-hydroxyphenyl)-propane, and mixtures thereof.

The polyamines can be aliphatic or aromatic. Aromatic diamines are preferred, like for instance 4,4'-diamino diphenyl methane.

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The amino alcohol can be aliphatic or aromatic. Aromatic amino alcohol are preferred like for instance, p-aminophenol.

The imides and amides can be aliphatic or aromatic. Heterocyclic imides and amides are preferred, like for instance 1,3,5-triazinetriol and imidazolidine-5,2,4-dione.

Polycarboxylic acids can be aliphatic or aromatic. An example of dimeric fatty acid is linoleic dimer acid. The polycarboxylic acid is preferably an aromatic dicarboxylic acid like for instance hexahydrophthalic acid.

### 1.3. Processes for making epoxy derivatives

10 The process for making epoxy resins, glycidyl ethers and glycidyl esters generally involve a reaction of the product containing epichlorohydrin and the compound containing at least one active hydrogen atom, followed by dehydrochlorination with a basic agent

15 The process for making epoxy resin usually involves two steps: the preparation of an uncured epoxy resin followed by a curing step.

#### 1.3.1. Uncured ER

The reaction between the product containing epichlorohydrin and the compound containing at least one, preferably two active hydrogen atoms can be carried out by any process known in the art like for instance the Caustic

20 Coupling Process and the phase-transfer catalyst process, for making Liquid Epoxy Resins (LER), the Taffy and the Advancement or Fusion process for making Solid Epoxy Resins (SER).

#### Caustic Coupling Process

25 In the caustic process, caustic is used as a catalyst for the nucleophilic ring-opening (coupling reaction) of the epoxide group on the primary carbon atom of epichlorohydrin by the phenolic hydroxyl group and as a dehydrochlorinating agent for conversion of the chlorhydrin to the epoxide group. Caustic (NaOH) can however be substituted by any basic compound.

30 The epichlorohydrin and the compound with active hydrogen atom, preferably an aromatic hydroxyl or aromatic amine compound, are employed in a molar ratio of from about 2:1 to about 10:1, preferably from about 2:1 to about 6:1, respectively.

35 The basic compound may be an organic or inorganic basic compound. Organic basic compounds are for example amines, phosphines and ammonium, phosphonium or arsonium hydroxides. Inorganic basic compounds are preferred. The expression "inorganic compounds" is understood to mean compounds which

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do not contain a carbon-hydrogen bond. The inorganic basic compound may be chosen from alkali and alkaline-earth metal oxides, hydroxides, carbonates, hydrogencarbonates, phosphates, hydrogenphosphates and borates, and mixtures thereof. Alkali and alkaline-earth metal oxides and hydroxides are preferred.

- 5 Preferred alkali metal hydroxides which can be employed herein include, for example, sodium hydroxide, potassium hydroxide, lithium hydroxide or mixtures thereof. Sodium hydroxide is especially preferred.

In the process according to the invention, the basic compound may be in the form of a liquid, an essentially anhydrous solid, a hydrated solid, an aqueous 10 and/or organic solution or an aqueous and/or organic suspension. The basic compound is preferably in the form of an essentially anhydrous solid, a hydrated solid, an aqueous solution or an aqueous suspension. It is preferred to use a solution or a suspension, preferably a solution of the basic compound, preferably sodium hydroxide, in water.

15 The content of the basic agent in the solution or suspension is generally higher than or equal to 5 % by weight, preferably higher than or equal to 10 % by weight, preferably higher than or equal to 20 % by weight, and most preferably higher than or equal to 30 % by weight. That content is usually lower than or equal to 70 % by weight, preferably lower than or equal to 60 % by weight, 20 preferably lower than or equal to 50 % by weight, and most preferably lower than or equal to 40 % by weight.

The alkali metal hydroxide is preferably employed as an aqueous solution, usually at a concentration of from about 20 to about 50, preferably from about 40 to about 50 percent by weight.

25 The amount of basic compound, preferably alkali metal hydroxide, which is employed in the process of the present invention is from about 0.80 mole to about 1.2 mole of basic agent, preferably from about 0.90 mole to 1.0 mole per each, preferably aromatic, hydroxyl group and, preferably aromatic, amine hydrogen.

30 The basic agent, epichlorohydrin and the compound containing active hydrogen atom can be mixed in any order. It is preferred to add the basic compound to a mixture of the two other reactants. The basic agent, preferably, alkali metal hydroxide can be added either continuously or incrementally, but never is all of the alkali metal hydroxide added in one increment.

35 The reaction can be carried out in a solvent. Suitable solvents which can be employed include any solvent which does not react with any component in the

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reaction mixture. Preferably such solvent is partially or wholly miscible with water, forms a codistillate with the epichlorohydrin and water and the distillate has a boiling point below that of the lowest boiling component of the reaction mixture at the pressure employed. Suitable such solvents include primary and

- 5 secondary alcohols such as, for example, 1-methoxy-2-hydroxy propane, 1-butoxy-2-hydroxy ethane, cyclohexanol. The secondary alcohols are preferred.

When a solvent is used, the amount of solvent which is employed will depend on the particular solvent and the compound containing active hydrogen atom being employed. The solvent generally ranges from about 5 to about

- 10 50 weight percent, preferably from about 10 to about 40 weight percent based on the total weight of reactants.

The pressure can be equal to 1 bar absolute, lower than 1 bar absolute or higher than 1 bar absolute. When a solvent is used, suitable pressures which can be employed are those which will provide the codistillate with a boiling point of from about 45 °C to about 80 °C, preferably from about 55 °C to about 70 °C.

- 15 The temperature of the reaction is usually greater than or equal to 25 °C, preferably greater than or equal to 50 °C, more preferably greater than or equal to 90 °C, and most preferably greater than or equal to 95 °C. The temperature of the reaction is usually lower than or equal to 200 °C, preferably lower than or equal to 150 °C, more preferably lower than or equal to 125 °C, and most preferably lower than or equal to 120 °C.

- 20 The reaction is usually conducted for a length of time such that the quantity of groups containing active hydrogen atom remaining in the reaction mixture is not greater than about 0.5, preferably not greater than about 0.2 percent by weight. That time is usually greater than or equal to 0.5 h, frequently greater than or equal to 1.0 h, often greater than or equal to 2.0 h, and most particularly greater than or equal to 3.0 h. The time of reaction is usually lower than or equal to 20 h, often lower than or equal to 10 h, frequently lower than or equal to 5 h, and most particularly lower than or equal to 4 h.

- 25 30 Upon completion of the reaction, the resultant epoxy resin is finished in any of the methods normally employed. The excess epichlorohydrin is usually removed by distillation and the salt removed by filtration, centrifugation and/or water washing.

- 35 The epichlorohydrin distillation is generally carried out in two steps. The first step is carried out generally at atmospheric pressure (1 bar absolute), at a temperature usually greater than or equal to 100 °C, preferably greater than or

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equal to 120 °C, more preferably greater than or equal to 130 °C, and most preferably greater than or equal to 145 °C and usually lower than or equal to 200 °C, preferably lower than or equal to 180 °C, more preferably lower than or equal to 175 °C, and most preferably lower than or equal to 155 °C. The second

- 5 step is carried out usually at a subatmospheric pressure, usually lower than or equal to 0.1 bar absolute, preferably lower than or equal to 0.01 bar, more preferably lower than or equal to 0.005 bar, and most preferably lower than or equal to 0.002 bar, at a temperature usually greater than or equal to 150 °C, preferably greater than or equal to 170 °C, more preferably greater than or equal to 190 °C, and most preferably greater than or equal to 195 °C and usually lower than or equal to 300 °C, preferably lower than or equal to 250 °C, more preferably lower than or equal to 220 °C, and most preferably lower than or equal to 215 °C.
- 10

15 The salt which is formed can be separated from the crude product through addition of a solvent, e.g. toluene, followed by filtration and distillation to remove the solvent.

#### Phase-Transfer Catalytic Process

Alternatively, in the Phase-Transfer Catalyst Process, the coupling reaction and dehydrochlorination can be performed separately by using phase-transfer coupling catalysts, such as quaternary ammonium salts, which are not strong enough bases to promote dehydrochlorination. Once the coupling reaction is completed, caustic is added to carry out the dehydrochlorination step. Via this method, higher yields of for example the monomeric diglycidyl ether of Bisphenol A (DGEBA) (> 90 %) are readily available.

- 20  
25 Batch methods and preferably continuous or semi continuous processes can be used.

#### Taffy Process

The Taffy method is used to prepare higher molecular weight solid resins. It is directly from epichlorohydrin, the compound containing active hydrogen atoms, and a stoichiometric amount of NaOH. This process is very similar to the caustic coupling process used to prepare liquid epoxy resins. Lower epichlorohydrin to compound containing active hydrogen atoms ratios are used to promote formation of high molecular weight resins. Upon completion of the polymerization, the mixture consists of an alkaline brine solution and a water-resin emulsion. The product is recovered by separating the phases, washing the resin with water, and removing the water under vacuum.

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The epichlorohydrin and the compound with active hydrogen atom, preferably an aromatic hydroxyl or aromatic amine compound, are employed in a molar ratio of from about 1:1 to about 2:1, preferably from about 1.3:1 to about 1.8:1, respectively.

5       The alkali metal hydroxide is preferably employed as an aqueous solution, usually at a concentration of from about 1 to about 20, preferably from about 5 to about 15 percent by weight.

10      The amount of basic compound, preferably alkali metal hydroxide, which is employed in the process of the present invention is from about 0.05 mole to about 2 mole of basic agent, preferably from about 0.1 mole to 0.5 mole per each, preferably aromatic, hydroxyl group and, preferably aromatic, amine hydrogen.

15      The temperature of the reaction is usually greater than or equal to 25 °C, preferably greater than or equal to 50 °C, more preferably greater than or equal to 90 °C, and most preferably greater than or equal to 95 °C. The temperature of the reaction is usually lower than or equal to 200 °C, preferably lower than or equal to 150 °C, more preferably lower than or equal to 125 °C, and most preferably lower than or equal to 120 °C.

20      The time of reaction is usually greater than or equal to 0.1 h, frequently greater than or equal to 0.5 h, often greater than or equal to 1.0 h, and most particularly greater than or equal to 1.5 h. The time of reaction is usually lower than or equal to 20 h, often lower than or equal to 10 h, frequently lower than or equal to 5 h, and most particularly lower than or equal to 4 h.

25      The basic agent, epichlorohydrin and the compound containing active hydrogen atom can be mixed in any order. It is preferred to add epichlorohydrin to a mixture of the two other reactants.

30      The reaction is usually carried out under vigorous agitation.

35      At the end of the reaction, the mixture separates into two layers. The heavier aqueous layer is drawn off and the molten, taffy-like product is washed with hot water until the wash water is neutral. The taffy-like product is dried at a temperature generally higher than or equal to 100 °C, preferably higher than or equal to 120 °C.

35      Alternatively, epichlorohydrin and water can be removed by distillation at temperatures up to 180 °C under vacuum. The crude resin/salt mixture can then be dissolved in a secondary solvent to facilitate water washing and salt removal.

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The secondary solvent can then be removed via vacuum distillation to obtain the product.

The advancement or fusion process is an alternative method for making solid epoxy resin and is based on the chain-extension reaction of liquid epoxy

5 resin (for example, crude DGEBA) with bisphenol A.

### 1.3.2. Curing agents

The curing of Epoxy Resins can be carried out using classical curing agents. The cure can be done with coreactive curing agents, or it can be catalytic or photoinitiated cationic.

10 The coreactive curing agents can be selected from amine functional curing agents, carboxylic functional polyester and anhydride curing agents, phenolic-terminated curing agents, melamine-, urea-, and phenol-formaldehyde resins, mercaptans (polysulfides and polymercaptans) curing agents, cyclic amidines curing agents, isocyanate curing agents and cyanate ester curing agents

15 The amine functional curing agents can be primary and secondary amines, polyamides, amidoamines and dicyandiamide.

The amines can be aliphatic, cycloaliphatic, aromatic amines or aryl amines.

20 The aliphatic amines can be selected from liquid aliphatic polyamines, such as polyethylene polyamines, hexamethylene diamine, polyether amines (polyglycol-based polyamines), ketimines (reaction products of ketones and primary aliphatic amines), Mannich base adducts (reaction products of amine, phenol and formaldehyde), polyetheramines (reaction product of polyols derived from ethylene or propylene oxide with amines) and mixtures thereof.

25 The cycloaliphatic amines can be selected from isophorone diamine, bis(4-amino-cyclohexyl)methane, 1,2-diamino-cyclohexane, trihexylmethylenediamines, metaxylylenediamine, and mixtures thereof.

The aromatic amines can be selected from meta-phenylenediamine, methylene dianiline, alkyl (tetraethyl-)substituted methylene dianiline, 4,4'-diaminodiphenylmethane, 4,4'-diamino diphenyl sulfone, diethylenetoluenediamine

The aryl amines can be selected from meta xylylenediamine, 1,3-bis(aminomethyl cyclohexane).

30 The amine can be more specifically selected from diethylenetriamine, triethylenetetramine, Poly(oxypropylene diamine), poly(oxypropylene triamine), poly(glycol amine), N-aminoethylpiperazine, isophorone diamine, 1,2-

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diaminocyclohexane, bis(4-aminocyclohexyl)methane, 4,4-diamino-diphenylmethane, 4,4-diaminodiphenyl sulfone, m-phenylenediamine, diethyltoluenediamine, meta-xylene diamine, 1,3-bis(aminomethyl) cyclohexane, and mixtures thereof.

5       The polyamides can be obtained by reaction of dimerized and trimerized vegetable oil fatty acids (9,12 and 9,11-linoleic acids) with polyamines (diethylene triamine) or from polyamines and phenolic-containing carboxylic acids (phenalkamines).

10      The amidoamines can be obtained by reaction of mono functional acid like tall-oil fatty acid with a polyamine such diethylenediamine.

15      The carboxylic functional polycster can be obtained by reaction of terphthalic acid, trimellitic anhydride and neopentyl alcohol

20      The acid anhydrides can be phthalic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, methyl hexahydrophthalic anhydride, hexahydrophthalic anhydride, nadic methyl anhydride or methyl himic anhydride, benzophenonetetracarboxylic dianhydride, tetrachlorophthalic anhydride, and mixtures thereof.

25      The phenolic-terminated curing agents are products that can be obtained by reaction of phenol, cresol or bisphenol a with formaldehydes.

30      The mercaptans (polysulfides and polymercaptans) curing agents generally contain terminal thiols.

35      The cyclic amidines curing agents can be for instance 2-phenyl imidazolidine.

40      The cyanate ester curing agents can be for instance bisphenol a dicyante ester.

45      The catalytic cure can be carried out with Lewis bases or Lewis acids.

50      The Lewis bases are for instance tertiary amine, like 2-diethylamino-methylphenol, 2,4,6-tris(dimethylaminomethyl)phenol and imidazoles such as 2-methylimidazole and 2-phenylimidazole, cyclic amidines like 2-phenylimidazoline, substituted ureas like 3-phenyl-1,1-dimethylurea and quaternary ammonium salt like tetralkyl- and alkyl-triphenyl phosphonium salts.

55      The Lewis acid can be selected from boron trifluorides, preferably boron trifluoride.

60      The Photoinitiated Cationic Cure can be carried out with photoinitiators like aryldiazonium salts, diaryldiazonium salts, diaryliodonium salts and onium

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salts of Group VIa elements, such as triarylsulfonium salt, dialkylphenacyl sulfonium salts.

#### 1.4 Uses of epoxy resins

The epoxy resins can be used in coating applications and in structural

- 5 applications. The coating applications can be in the fields of marine and industrial maintenance (corrosion-resistant coatings for ships, shipping containers, offshore oil rigs and platforms, transportation infrastructures such as bridges, rail car coatings, coatings for industrial storage tanks, and primers for light industrial and agricultural equipment), metal container (aluminum and steel food and beverage cans) and coil coatings (metal can ends, can bodies, building products, appliance panels, transportation, and metal furniture applications), automotive coatings (primer surface coatings) and inks and resists. Coating can be done using various technologies like low solids solventborne coating, high solid solventborne coating, solvent-free coating, waterborne coating, powder coating and radiation-curable coating.
- 10
- 15

The structural applications can be in the field of structural composites (fiber reinforcing materials based on glass, boron, graphite and aromatic polyaramides), of civil engineering, flooring (floor paints, self-leveling floors, trowelable floors, and pebble-finished floors) and construction, of electrical

- 20 laminates, of electrical laminates (printed wiring boards and printed circuit boards), of other electrical and electronic applications, like casting, potting, encapsulation (switchgear components, transformers, insulators, high voltage cable accessories, and similar devices) and transfer molding (encapsulation of electronic components such as semiconductor chips, passive devices, and integrated circuits), of adhesives (cohesion between similar and dissimilar materials such as metals, glass, ceramics, wood, cloth, and many types of plastics) and of tooling (prototypes, master models, molds and other parts for aerospace, automotive, foundry, boat building, and various industrial molded items).
- 25
- 30

#### 1.5 Uses of Glycidyl Ethers and Esters

These products are used for applications such as coatings, adhesives and reactive diluents.

#### 1.6 Uses of Glycidyl amides and imides

These products are used for applications such as outdoor powder coatings

- 35 with polyesters, or in applications in which a non-yellowing epoxy resin is desirable.

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## 2. PRODUCTS FOR FOOD-DRINK APPLICATIONS - COAGULANTS

### 2.1. General

The product containing epichlorohydrin according to the invention can be used for the manufacture of products that will be used in applications where they will come in contact with food and drink, more specifically for the manufacture of synthetic organic coagulants.

Coagulation refers to the reduction or elimination of electrostatic repulsion forces between particles via addition of certain coagulants, and in technical terms, the first phase of floc formation after chemical mixing and destabilization, but before dosing of flocculants.

Coagulants are generally polymers with a high cationic charge density to neutralize negative charges of colloids and initiate the formation of flocs. They generally exhibit a relatively low molecular weight in order to permit a good diffusion of the charges around the particles and a low viscosity to allow a good distribution of the polymer in the effluents.

By coagulant, one intends to denote a polymer, comprising at least one repeat unit containing at least one 2-hydroxypropylalkylammonium group.

An example of a coagulant molecule is presented in Figure 8.

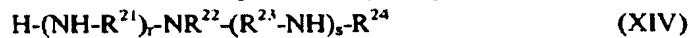
### 2.2. Co-reactants

In the application according to the invention, the product containing epichlorohydrin is usually subjected to a reaction with ammonia, an amine, a polyaminoamide or a polyimine.

The amine can be a mono-, a di- or a polyamine. The amine can be aliphatic, alicyclic or aromatic, saturated or unsaturated, linear or substituted.

The amine has preferably at least one, more preferably at least two primary amino hydrogens.

The amine can be represented by the general formula:



wherein R<sup>22</sup> and R<sup>24</sup> can be equal, except when equal to H, or different and can independently be selected from H, alkyl or alkenyl radical, linear, branched or carbocyclic, having from 1 to 30 carbon atoms, R<sup>21</sup> and R<sup>23</sup> can be equal or different, preferably equal, divalent aliphatic radical aromatic radicals having from 2 to 12 carbon atoms, each of r and s is an integer of from 0 to 6, r plus s equals 0 to 6.

Amines include lower alkyl and lower alkenyl primary monoamines, such as methylamine, ethylamine, isopropylamine, tertbutylamine, mixed

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amylamines, n-octylamine, branched-chain nonylamine, secondary amines such as dimethylamine, ethylmethylamine, diethylamine, propylmethylamine, propylethylamine, dipropylamine, dibutylamine, propylbutylamine, ethylbutylamine, methylbutylamine, pentylethylamine, pentylmethyamine, and

5 pentylpropylamine, tertiary amines, as well as alkylendiamines, triamines and polyamines, with or without an alkenyl or alkyl substituent bonded to nitrogen, such as ethylenediamine, propylenediamine, butylenediamine, pentylenediamine, hexylenediamine, octylenediamine, dodecylenediamine, cyclohexylenediamine, diethylenetriamine, dipropylenetriamine, dipentenylenetriamine, triethylene

10 tetramine, tributylenetetramine, trihexylenetetramine, tetraethylenepentamine, tetrapropylcncpcntamine, pentahcxylcnchcxamine, pentapropylcnchcxamine, N-ethyl-1,2-ethylenediamine, N-(2-propenyl)-1,3-propanediamine, N-hexyl-1,4-butanediamine, N-2ethylhexyl-1,3-propanediamine, N-(5-octenyl)-1,6-

15 hexanediamine, N-butyltriethylenetriamine, N-hexyltripropylenetetramine, N-nonyltetrabutylenepentamine and N-(oleyl)-hexaethyleneheptamine, N-alkyl-1,3-diaminopropane, butane and hexane, where the radical alkyl can be hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, and tetracosyl.

20 The monoamine is preferably a secondary amine, more preferably dimethylamine.

The diamine is more preferably selected from 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane, a N-substituted diaminopropane, more preferably, 1-amino-3-dimethylaminopropane, 1-amino-3-diethylaminopropane, 25 1-amino-3-cyclohexylaminopropane, N,N,N',N'-tetramethyl-1,3-propanediamine, 1,3-diarninobutane, 1,5-diaminopentane, 1,8-diaminoctane, 1,10-diaminodecane, 1,12-diaminododecane, 2-(diethylamino)ethylamine, 1-diethylamino-4-aminopentane, 3-aminomethyl-3,5,5-trimethylcyclohexylamine and N,N,N',N'-tetramethyl-1,6-hexanediamine.

30 Polyaminoamides are generally obtained from polyamide, preferably polyacrylamide, formaldehyde and an amine, preferably a secondary amine. Poly[N-(dialkylaminoalkyl)acrylamide] is particularly preferred.

Polyimines are usually obtained by ring opening polymerization of alkylene imine, preferably ethylene imine.

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### **2.3. Processes**

The reaction between the product containing epichlorohydrin and the compound containing at least one, preferably two primary amino hydrogens can be carried out by any process known in the art.

5        The reaction is generally carried out in the liquid phase, possibly in the presence of a solvent. The solvent may be selected from water, an organic solvent, preferably miscible with water, or mixtures thereof. Water is preferred. Monoalcohols, like methanol, ethanol, n-propanol, isopropanol and butanol are preferred organic solvents

10      When a solvent is used, the ammonia or amine content in the solvent-ammonia or amine mixture is usually higher than or equal to 5 % by weight (% wt), preferably higher than or equal to 10 wt %, more preferably higher than or equal to 20 wt % and most preferably higher than or equal to 45 wt %. That content is usually lower than or equal to 90 wt %, preferably lower than or equal to 75 wt %, more preferably lower than or equal to 60 wt %, and most preferably lower than or equal to 55 wt %.

15      The molar ratio between epichlorohydrin and ammonia or amine is generally higher than or equal to 0.1, preferably higher than or equal to 0.5, more preferably higher than or equal to 0.75 and most preferably higher than or equal to 1. That ratio is usually lower than or equal to 10, preferably lower than or equal to 5, more preferably lower than or equal to 3, and most preferably lower than or equal to 2.

20      The temperature at which the reaction is carried out is generally higher than or equal to 10 °C, preferably higher than or equal to 25 °C, more preferably higher than or equal to 50 °C and most preferably higher than or equal to 60 °C. That temperature is usually lower than or equal to 120 °C, preferably lower than or equal to 110 °C, more preferably lower than or equal to 100 °C, and most preferably lower than or equal to 90 °C.

25      The pressure at which the reaction is carried out is generally higher than or equal to 0.1 bar absolute, preferably higher than or equal to 0.2 bar, more preferably higher than or equal to 0.5 bar and most preferably higher than or equal to 1 bar. That pressure is usually lower than or equal to 20 bar, preferably lower than or equal to 10 bar, more preferably lower than or equal to 5 bar, and most preferably lower than or equal to 2 bar.

30      The duration of the reaction is generally higher than or equal to 10 min absolute, preferably higher than or equal to 20 min, more preferably higher than

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or equal to 30 min and most preferably higher than or equal to 60 min. That duration is usually lower than or equal to 10 h, preferably lower than or equal to 5 h, more preferably lower than or equal to 3 h, and most preferably lower than or equal to 2 h.

- 5        The manufacturing procedure usually involves the dissolution of the amines or ammonia in the solvent, followed by a slow addition of the epichlorohydrin, itself possibly dissolved in a solvent, possibly cooling in order to keep the temperature of the reaction between 10 and 50 °C, often between 25 and 40 °C, then after the epichlorohydrin addition is complete, raising the 10 temperature to between 60 and 90 °C.

The reaction product can be recovered as an aqueous solution, or a solid after further treatments, e.g. distillation of the solvents under vacuum, treatment of the solution with an acid or a base.

- 15      These reactions lead to the formation of the monomer. For example a reaction between epichlorohydrin and dimethylamine produces the epichlorohydrin dimethylamine monomer. This is then homopolymerized to the corresponding quaternary ammonium compound which is a low molecular weight cationic polymer used as a coagulant. Such polymerization usually takes place under alkaline conditions.

- 20      The monomer can also be copolymerized with acrylamide to produce higher molecular weight polymers also used for water treatment.

#### 2.4. Products characteristics

- 25      The obtained polymers usually exhibit a molecular weight that is higher than or equal to 5 000, often higher than or equal to 10 000, and frequently higher than or equal to 50 000. That molecular weight is usually lower than or equal to 500 000, often lower than or equal to 400 000, and frequently lower than or equal to 300 000. They can be obtained as aqueous solution containing from 40 to 50 % by weight of polymers and exhibiting viscosities from 40 to 11 000 centipoise.

#### 30      2.5. Uses

These polymers can be used for treatment of raw water for conversion to drinking water, for recycling paper of water in Pulp & Paper Industry, for paint deactivation, for breaking oil emulsions, for oil and grease removal, and for sludge dewatering. They can also be used for sugar refining.

**3. PRODUCTS FOR FOOD-DRINK APPLICATIONS – WET-STRENGTH RESINS**

**3.1. General**

The product containing epichlorohydrin according to the invention can be used for the manufacture of products that will be used in applications where they will come in contact with food and drink, more specifically for the manufacture of wet-strength resins.

By wet-strength resin one intends to denote a polyaminoamide polymer, the chemical formula of which contains at least one group selected from 2,3-epoxypropylamine, 2,3-epoxypropylammonium, 3-chloro-2-hydroxypropylamine, 3-chloro-2-hydroxypropylammonium, 3-hydroxyazetidinium, and any combination of at least two of them.

Examples of chemical formulas of such a polymer are presented in Figure 9.

**3.2. Co-reactants**

In the application according to the invention, the product containing epichlorohydrin is usually subjected to a reaction with a polyamine or a polyamide.

The polyamine and the reactions conditions are as described above for the manufacture of coagulants.

The polyamide is usually obtained by reacting an amine, preferably a polyalkylene polyamine (in this case the polyamide is generally referred as a polyaminamide) and a dicarboxylic acid, preferably a saturated aliphatic dicarboxylic acid, as described in US 865,727, the content of which is incorporated herein by reference. The polyamide may be represented by the general formula



where  $\text{R}^{21}$ ,  $\text{R}^{22}$ ,  $\text{R}^{23}$ ,  $r$  and  $s$  are as described above, and  $\text{R}^{24}$  is the divalent hydrocarbon radical of the dibasic carboxylic acid, preferably selected from phenylene, naphthalene, methylene, ethylene, propylene, butylenes, pentylene, hexylene, octylene and nonylene.

Preferably, the polyamide may be represented by the general formula



wherein  $t$  and  $x$  are each 2 or more and wherein

the  $-\text{NH}(\text{C}_2\text{H}_2\text{HN})_x\text{-}$  group is derived from the polyamines described above, preferably containing from 2 to 8 alkylene groups, more preferably from

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diethylenetriamine, triethylenetetramine, tetraethylenepentamine, dipropylenetriamine and N-bis(aminopropyl)methylamine the -COR<sup>24</sup>CO- group is derived from dibasic carboxylic acid containing from 2 to 12 carbon atoms, preferably selected from phenylene, naphthalene, methylene, 5 ethylene, propylene, butylenes, pentylene, hexylene, octylene and nonylene. The acid is more preferably selected from malonic, succinic, glutaric, adipic, diglycolic, sebacic or azelaic acid, and mixtures thereof.

### 3.3. Processes

The reaction between the polyamide and epichlorohydrin is usually carried 10 out at a temperature generally higher than or equal to 45 °C. That temperature is usually lower than or equal to 100 °C, preferably lower than or equal to 70 °C. The temperature at which the reaction is conducted is preferably selected in two stages. In the first stage, the reaction mixture is maintained at 30 °C -50 °C., 15 preferably 39 ° - 41 °C. Reaction time for the first stage is preferably about 90-190 minutes to form an intermediate polyaminochlorohydrin. Then the reaction temperature is gradually increased to 55 ° -75 °C. such that the intermediate polyaminochlorohydrin is controllably cross-linked to a determined level. The second stage is continued until the viscosity of the reaction mixture reaches the desired level ( preferably level M to N on a Gardner-Holdt viscosity scale).

Broadly speaking, the reaction can be carried out neat or in an aqueous 20 solution of up to 57 wt % in water. Preferably, the polyaminoamide is reacted with epichlorohydrin in an aqueous solution of 52-57 wt % in water that is, a solution of 43-48 wt % total solids (the weight percentage of the solution that is solubilized solid material), more preferably about 45 wt % total solids. Reaction 25 time varies depending on the temperature, with lower temperatures taking longer times. The typical composition of these resins is 12.5% (10-40% solids). However, due to the cost of transporting water, companies have tried to produce resin solutions of higher concentration. It appears that at least one of the main 30 issues making such concentrated solutions difficult to prepare is their high content of dichloropropanol so the level of this impurity is exceeded in the final application.

Reaction is preferably carried out until all, or substantially all of the 35 available amine groups on the polyaminoamide are reacted with epichlorohydrin. Generally, reaction times vary between about 1 and 19 hours, preferably between 3 and 6 hours. Because the reaction is exothermic, the epichlorohydrin is added slowly over time to the polyaminoamide to allow for more effective heat transfer

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from the reaction medium. Heat transfer from the reaction medium can be accomplished according to known procedures, such as immersing the reaction vessel in a refrigerated environment, e.g., an ice bath, or passing refrigerated coils inside the reaction vessel.

5       The reaction is usually carried out in aqueous solution to moderate the reaction. The pH adjustment is usually not necessary but since the pH decreases during the reaction, it may be desirable in some cases, to add alkali to combine with at least some of the acid formed.

10      In the reaction, it is preferred to use sufficient epichlorohydrin to convert the entire secondary amine group to tertiary amine groups. The molar ratio between epichlorohydrin and the secondary amine groups is usually higher than or equal to 0.1, preferably higher than or equal to 0.5, and more preferably higher than or equal to 1. That molar ratio is usually lower than or equal to 10, preferably lower than or equal to 5, and more preferably lower than or equal to 2.

15      The reaction between the polyamide and epichlorohydrin can also be carried in the presence of a quaternizing agent, the conditions of reaction and the reactants, except for the inclusion of the quaternizing agent, being essentially the same as described above. In a preferred procedure, the epichlorohydrin is first added to an aqueous solution of the polyamide at a temperature from 45 to 55  
20      °C. The reaction mixture is then heated to a temperature from about 60 to 100 °C, and preferably from about 50 to 80 °C, depending on the rate of the polymerization desired. After a suitable time at that temperature, i.e., 0 to 100 min, a time after which the epoxy group of the epichlorohydrin have reacted with the secondary amine groups of the polyamide, the quaternizing agent is added  
25      and the reaction mixture heated, preferably at a temperature from 60 °C to 80 °C. The pH of the reaction mixture is then reduced to 4, preferably between 2 and 3 with any suitable acid such as sulphuric, hydrochloric formic and the like. The amount of quaternizing agent should be sufficient to convert from 25 % to 75 %, preferably 50 % of the tertiary amine group to quaternary group.

30      The quaternizing agent may be any compound capable of quaternizing a tertiary nitrogen atom in an aqueous medium. In general these compounds are characterized by having as a principal part of their structure an alkyl group or substituted alkyl group which is readily available for alkylation under the conditions herein described. These include the lower alkyl esters of mineral  
35      acids such the halides, sulfates and phosphates, and substituted alkyl halides. Illustrative of these compounds which may be used are dimethyl, diethyl and

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dipropylsulfate, methyl chloride, methyl iodide, methyl bromide, ethyl bromide, propyl bromide, the mono-, di- or tri-methyl, ethyl and propyl phosphates, 1,3-dichloropropanol-2 and 1-chloroglycerol. Certain aromatic compounds may also be used like benzyl chloride and methyl p-toluene sulfonate.

- 5        The above products resulting from the reaction between epichlorohydrin and the polyamide can be further cross polymerized by treatment with a sodium carbonate or sodium hydroxide solution at a pH between 10.5 and 12.

#### 3.4. Uses

- 10      These resins are used in papers that will get wet such as paper towels, tea bags, coffee filters, milk cartons, meat wrapping, wallpaper. They can also be used in the production of high fructose corn syrup and to prevent wool from shrinking.

### 4. CATIONIZATION AGENTS

#### 4.1. General

- 15      The product containing epichlorohydrin according to the invention can be used for the manufacture of cationization agents.

By cationization agent, one intends to denote a quaternary ammonium salt, the chemical formula of which contains at least one group selected from 2,3-epoxypropyl, 3-chloro-2-hydroxypropyl, and their combination, and which is not a polymer.

Cationization agents are often quaternary ammonium salt containing a glycidyl or a 3-chloro-2-hydroxypropyl group attached to the nitrogen atom. The cationization agent can be isolated as solids or as solution in water or in organic solvents.

- 25      Examples of cationization agents are 3-chloro-2-hydroxypropyl trimethylammonium chloride and glycidyl trimethyl ammonium chloride.

#### 4.2. Co-reactants

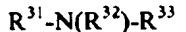
- 30      In the application according to the invention, the product containing epichlorohydrin is usually subjected to a reaction with an amine, an amine salt, or a mixture thereof.

The amine is preferably a tertiary amine and the amine salt is preferably a tertiary amine salt.

The tertiary amine salt is for instance a salt obtained by treating an amine with an acid, preferably an inorganic acid, like for instance hydrochloric or sulphuric acid.

The tertiary amine may be represented by the formula

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(XVII)

wherein R<sup>31</sup>, R<sup>32</sup> and R<sup>33</sup> can be selected from the group consisting of alkyl, cycloalkyl, alkene, aryl, aralkyl, alkylaryl, two of them being possibly joined to form a ring and containing from 1 to 25 carbon atoms. The group attached to the nitrogen can be linear or substituted, saturated or unsaturated.

If all three of R<sup>31</sup>, R<sup>32</sup> and R<sup>33</sup> are the same, they preferably each should not contain more than 4 carbon atoms. If all three of R<sup>31</sup>, R<sup>32</sup> and R<sup>33</sup> are not the same and if R<sup>33</sup> contains up to 18 carbon atoms, the R<sup>31</sup> and R<sup>32</sup> should preferably be of the group consisting of methyl and ethyl. If R<sup>31</sup> and R<sup>32</sup> are joined to form a ring, then R<sup>33</sup> should preferably be from the group consisting of methyl and ethyl.

Examples of suitable tertiary amines are triethylamine, N-methyl and N-ethylmorpholine, N-ethyl and N-methylpiperidine and methyl diallylamine, trimethylamine, dimethylbenzylamine, dimethyldodecylamine, 15 dimethylstearylamin es, dimethylaniline, tri-npropylamine.

It is particularly preferred that the tertiary amine possess two methyl groups attached to the nitrogen, like for instance, trimethylamine, dimethylbenzylamine, dimethyldodecylamine, dimethylstearylamine, and dimethylaniline.

20 The amine salt is preferably a salt obtained by reaction between the above described amines with hydrochloric or sulfuric acid, preferably with hydrochloric acid.

#### 4.3. Processes

25 The reaction between the product containing epichlorohydrin and the amine or the amine salt can be carried out by any process known in the art such as those described in US 2,876,217 the content of which is incorporated herein by reference.

30 The reaction is generally carried out in the liquid phase, possibly in the presence of a solvent. The solvent may be selected from water, an organic solvent e.g. an alcohol, a ketone, an ester or an aliphatic hydrocarbon, preferably miscible with water, or mixtures thereof. Water is preferred. Monoalcohols, like methanol, ethanol, n-propanol, isopropanol and butanol are preferred organic solvents, with methanol being particularly preferred.

35 The content of epichlorohydrin in the solvent is usually higher than or equal to 0.1 mol/l, often higher than or equal to 0.5 mol/l, frequently higher than or equal to 1.0 mol/l, particularly higher than or equal to 2 mol/l, specifically

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higher than or equal to 5 mol/l and sometimes higher than or equal to 10 mol/l.

That epichlorohydrin content is usually lower than 20 mol/l.

The content of amine or amine salt in the solvent is usually higher than or equal to 0.1 mol/l, often higher than or equal to 0.5 mol/l, frequently higher than or equal to 1.0 mol/l, particularly higher than or equal to 2 mol/l, specifically higher than or equal to 5 mol/l and sometimes higher than or equal to 10 mol/l.

That amine or amine salt content is usually lower than 20 mol/l.

The molar epichlorohydrine/amine or amine salt ratio is usually higher than or equal to 0.1, preferably higher than or equal to 0.5, more preferably

higher than or equal to 1 and most preferably higher than or equal to 1.2. That ratio is usually lower than or equal to 10, more preferably lower than or equal to 5 and least preferably lower than or equal to 2.

The temperature at which the reaction is carried out is generally higher than or equal to 0 °C, preferably higher than or equal to 10 °C, more preferably

higher than or equal to 25 °C and most preferably higher than or equal to 40 °C. That temperature is usually lower than or equal to 100 °C, preferably lower than or equal to 80 °C, more preferably lower than or equal to 60 °C, and most preferably lower than or equal to 50 °C.

The pressure at which the reaction is carried out is generally higher than or

equal to 0.1 bar absolute, preferably higher than or equal to 0.2 bar, more preferably higher than or equal to 0.5 bar and most preferably higher than or equal to 1 bar. That pressure is usually lower than or equal to 20 bar, preferably lower than or equal to 10 bar, more preferably lower than or equal to 5 bar, and most preferably lower than or equal to 2 bar.

The duration of the reaction is generally higher than or equal to 10 min

absolute, preferably higher than or equal to 20 min, more preferably higher than or equal to 30 min and most preferably higher than or equal to 60 min. That duration is usually lower than or equal to 72 h, preferably lower than or equal to 60 h, more preferably lower than or equal to 48 h, and most preferably lower

than or equal to 10 h.

When an amine salt or a mixture of an amine and of an amine salt is used, the pH of the reaction is usually at least 5, and preferably at least 6. That pH is usually at most 9, preferably at most 8.

In a first embodiment, the manufacturing procedure usually involves the

mixing of the amine, epichlorohydrin and water, followed by heating at the desired temperature for the desired duration. The aqueous solution is further

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concentrated by vacuum distillation. The temperature of distillation is as described for the reaction. The distillation pressure is usually lower than or equal to 100 mbar absolute, preferably lower than or equal to 75 mbar and most preferably lower than or equal to 50 mbar. That pressure is usually higher than or equal to 1 mbar absolute.

In a second embodiment, an aqueous solution of the amine is first added to hydrochloric acid until a pH between 8 and 9 is obtained. Epichlorohydrin is further added to the resulting solution and the mixture stirred at the desired temperature for the desired duration. The solution is further distilled under vacuum to the solid 3-chloro-2-trialkylammonium chloride. The solid can be used as such or further cyclized into the glycidyl derivative by reaction with sodium hydroxide in aqueous solution.

In a third embodiment, an amine hydrochloride is dispersed in water. Sufficient sodium hydroxide is added to raise the pH from around 3 to around 8. Epichlorohydrin is further added to the resulting solution and the mixture stirred at the desired temperature for the desired duration. The chlorohydrin group is further cyclized into the glycidyl derivative by reaction with sodium hydroxide in aqueous solution.

In the various embodiments, the aqueous solution obtained at the end of the reaction can be further concentrated by vacuum evaporation or distillation at a temperature of less than 50 °C in order to obtain a slurry containing at least 90 % by weight of solid, preferably at least 95 % by weight. A water miscible alcohol having 3 to 4 carbon atoms, such as isopropanol, n-propanol, and tert-butanol, preferably isopropanol, is added to the slurry, such as to obtain an alcohol content from 10 to 70 % wt, preferably from 25 to 50 % wt, based on the total weight of the resulting alcohol-water slurry. The precipitated solids are then recovered by filtration or by other means suitable for removing solids from liquid. The solid may optionally be washed with additional volumes of alcohol or another non-solvent and/or dried to remove any trace of water and alcohol.

The reaction product can be recovered as an aqueous solution, or a solid after further treatments, e.g. distillation of the solvents under vacuum, treatment of the solution with an acid or a base.

#### 4.4. Uses

Cationization agents are mainly used in the cationization of starch to be utilized by the paper industry for processing of high quality paper grades or for cationization of textile for dye fixing.

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## 5. FLAME RETARDANTS

### 5.1. General

The product containing epichlorohydrin according to the invention can be used for the manufacture of flame retardants additives.

- 5 The product containing epichlorohydrin according to the invention can preferably be used for the manufacture of phosphorus containing flame retardants additives.

By phosphorus containing flame retardants, one intends to denote a compound, the chemical formula of which contains at least one phosphorus atom 10 and at least one group selected from 2,3-epoxypropoxyloxy, 3-chloro-2-hydroxypropyl, and the combination of at least two of them.

Examples of chemical formulas for such compounds are presented in Figure 10.

### 5.2. Co-reactants

15 In the application according to the invention, the product containing epichlorohydrin is usually subjected to a reaction with an inorganic or organic compound containing phosphorus. Such inorganic compounds are for instance a phosphoric acid (ortho, pyro and polyphosphoric acid), a phosphoric acid salt and a phosphorus oxychloride. Examples of organic compounds containing phosphorus are for instance phosphoric acid esters (of ortho, pyro and 20 polyphosphoric acid), phosphonic acids, their esters or their salts, phosphinic acids, their esters or their salts and phosphine oxides.

The compounds containing phosphorus may be represented by the general formula



or



wherein  $X^1$ ,  $X^2$ ,  $X^3$  can independently be selected from a halogen, H, OH, OR<sup>41</sup>, R<sup>41</sup>, OR<sup>42</sup>(OH)<sub>n</sub> and R<sup>42</sup>(OH)<sub>n</sub>

30 wherein the halogen is preferably selected from bromine and chlorine and is preferably chlorine

wherein R<sup>41</sup> is an alkyl, an aryl, an alkylaryl, an arylalkyl, a cycloalkyl radical containing from 1 to 20 carbon atoms, often from 3 to 12 carbon atoms

wherein R<sup>42</sup> is an alkylene, arylene, alkylarylene, arylalkylene, cycloalkylene 35 radical containing from 1 to 20 carbon atoms, often from 3 to 12 carbon atoms wherein n is an integer equal to 1 or 2

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wherein at least two of X<sup>1</sup>, X<sup>2</sup>, X<sup>3</sup> can be joined to form a ring, preferably with the phosphorus atom.

Examples of phosphorus containing compounds are tris(1,3-dichloro-2-propyl) phosphate, tris(1-chloro-2-propyl) phosphate, tris(2,3-dichloropropyl) phosphate, isobutylbis(hydroxypropyl)phosphine oxide, 10-(2',5'-dihydroxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DHQEP), 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), the reaction products of DOPO and 4,4'-dihydroxybenzophenone (DOPO2OH and 2DOPO-PhOH, II as represented in Liu Y.L., Journal of Polymer Science: Part A: Polymer Chemistry, 2002, Vol. 40, 359-368 and Journal of Applied Polymer Science, 2002, Vol. 83, 1697-1701).

### 5.3. Processes

The reaction between the product containing epichlorohydrin and the phosphorus containing compound is carried out by any process known in the art such as those described in Journal of Applied Polymer Science, 2002, Vol. 83, 1697-1701).

The reaction is generally carried out in the liquid phase, possibly in the presence of a solvent. The solvent may be selected from water, an organic solvent e.g. an alcohol, or mixtures thereof. An alcohol is preferred.

20 Monoalcohols, like methanol, ethanol, n-propanol, isopropanol and butanol are preferred organic solvents, with ethanol being particularly preferred.

The content of epichlorohydrin in the reaction mixture is usually higher than or equal to 0.1 mol/l, often higher than or equal to 1.0 mol/l, frequently higher than or equal to 2 mol/l and particularly higher than or equal to 5 mol/l.

25 That epichlorohydrin content is usually lower than 20 mol/l.

The content of the phosphorus containing compound in the reaction mixture is usually higher than or equal to 0.1 mol/l, often higher than or equal to 0.2 mol/l and frequently higher than or equal to 0.5 mol/l. That content is usually lower than 2 mol/l.

30 The molar epichlorohydrin/ phosphorus containing compound ratio is usually higher than or equal to 1, preferably higher than or equal to 2, more preferably higher than or equal to 5 and most preferably higher than or equal to 10. That ratio is usually lower than or equal to 50, more preferably lower than or equal to 30 and most preferably lower than or equal to 20.

35 The temperature at which the reaction is carried out is generally higher than or equal to 0 °C, often higher than or equal to 5 °C, frequently higher than

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or equal to 10 °C, particularly higher than or equal to 20 °C and more specifically higher than or equal to 50 °C. That temperature is usually lower than or equal to 100 °C, preferably lower than or equal to 80 °C, more preferably lower than or equal to 60 °C, and most preferably lower than or equal to 30 °C.

5       The pressure at which the reaction is carried out is generally higher than or equal to 0.1 bar absolute, preferably higher than or equal to 0.2 bar, more preferably higher than or equal to 0.5 bar and most preferably higher than or equal to 1 bar. That pressure is usually lower than or equal to 20 bar, preferably lower than or equal to 10 bar, more preferably lower than or equal to 5 bar, and most preferably lower than or equal to 2 bar.

10      The duration of the reaction depends on the temperature at which the reaction is carried out. That duration is generally higher than or equal to 10 min absolute, preferably higher than or equal to 1 h, more preferably higher than or equal to 10 min and most preferably higher than or equal to 24 h. That duration is usually lower than or equal to 72 h, preferably lower than or equal to 60 h, more preferably lower than or equal to 48 h, and most preferably lower than or equal to 30 h.

15      A basic compound, e.g., potassium hydroxide can be present in the reaction medium. This is generally the case when the phosphorus containing compound includes OH groups in the molecule. The molar basic compound/phosphorus containing compound ratio is usually higher than or equal to 0.1, preferably higher than or equal to 0.15, and most preferably higher than or equal to 0.2. That ratio is usually lower than or equal to 5, more preferably lower than or equal to 3 and most preferably lower than or equal to 1.

20      An onium salt, preferably a quaternary ammonium or phosphonium salt, more preferably a quaternary ammonium chloride, like for instance benzyltrimethylammonium chloride, can be present in the reaction medium. This is generally the case when the phosphorus containing compound is a phosphine oxide. The onium/phosphorus containing compound ratio is usually higher than or equal to 0.01, preferably higher than or equal to 0.05, and most preferably higher than or equal to 0.1. That ratio is usually lower than or equal to 1, more preferably lower than or equal to 0.5 and most preferably lower than or equal to 0.2.

25      The product of the reaction can be recovered by any means, e.g., filtration and submitted to washing operations before being submitted to evaporation under reduced pressure.

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#### 5.4. Uses

Flame retardants are usually used to inhibit the evolution of combustible gases in various materials such as polymers, in particular in polyurethane foams.

### 6. DETERGENT INGREDIENTS

#### 5    6.1. General

The product containing epichlorohydrin according to the invention can be used for the manufacture of detergent ingredients. By detergent ingredient, one intends to denote a compound, the chemical formula of which contains at least one 3-sulfonate-2-hydroxy-propoxy group. The compound can be an oligomer or a polymer. An oligomer is a polymer with a number of repeat units in each polymer molecule of less than 20.

By detergent ingredient, one intends to denote a polymer, at least one repeat unit of which comprises at least one 2-hydroxypropylammonium group, preferably a 2-hydroxypropylimidazolidinium group.

15    The product containing epichlorohydrin according to the invention can preferably be used for the manufacture of cationic monomers, polymers or oligomers, anionic surfactants, for instance sulfonates based surfactants, preferably alkyl glycetyl ether sulfonate surfactants, monomeric or oligomeric or cationic cyclic amine based polymers.

#### 20    6.2. Co-reactants

In the application according to the invention, when the detergent auxiliary is a sulfonate based surfactant, the product containing epichlorohydrin is usually subjected to a reaction with an aliphatic alcohol containing from 10 to 40 carbon atoms, preferably from 10 to 22 carbon atoms more preferably from 14 to

25    18 carbon atoms and most preferably from 16 to 18 carbon atoms. The alkyl chain may be branched or linear or ethoxylated, wherein when present, the branches comprise an alkyl moiety containing from 1 to 4 carbon atoms, such as methyl or ethyl.

30    In the application according to the invention, when the detergent ingredient is a cationic amine based polymer, the product containing epichlorohydrin is usually subjected to a reaction with an amine selected from the group consisting of linear alkylamines, branched alkylamines, cycloalkylamines, alkoxyamines, amino alcohols, cyclic amines containing at least one nitrogen atom in a ring structure, alkylendiamines, polyetherdiamines, polyalkylenepolyaminesamine.

35    Specific examples of the said amines are given above.

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Cyclic amines containing at least one nitrogen atom in a ring structure are for example monoaminoalkylpiperazines, bis(aminoalkyl)piperazines, monoaminoalkylimidazoles, aminoalkylmorpholines, aminoalkylpiperidines and aminoalkylpyrrolidines. The monoaminoalkylpiperazines are for example 1-(2-

- 5 aminoethyl)piperazine and 1-(3-aminopropyl)piperazine. Preferred monoaminoalkylimidazoles have 2 to 8 carbon atoms in the alkyl group. Examples of suitable compounds are 1-(2-aminoethyl)imidazole and 1-(3-aminopropyl)imidazole. Suitable bis(aminoalkyl)piperazines are for example 1,4-bis(2-aminoethyl)piperazine and 1,4-bis(3-aminopropyl)-piperazine.

- 10 Preferred aminoalkylmorpholines are aminoethylmorpholine and 4-(3-aminopropyl)-morpholine. Other preferred compounds of this group are aminoethylpiperidine, aminopropylpiperidine and aminopropylpyrrolidine.

Cyclic amines with at least two reactive nitrogen atoms in the ring are for example imidazole, C-alkyl substituted imidazoles having 1 to 25 carbon atoms

- 15 in the alkyl group such as 2-methylimidazole, 2-ethylimidazole, 2-propylimidazole, 2-isopropylimidazole and 2-isobutylimidazole, imidazoline, C-alkyl substituted imidazolines having 1 to 25 carbon atoms in the alkyl group and arylimidazolines such as 2-phenylimidazoline and 2-tolylimidazoline, piperazine, N-alkylpiperazines having 1 to 25 carbon atoms in the alkyl group such as 1-  
20 ethylpiperazine, 1-(2-hydroxy-1-ethyl)piperazine, 1-(2-hydroxy-1-propyl)piperazine, 1-(2-hydroxy-1-butyl)piperazine, 1-(2-hydroxy-1-pentyl)piperazine, 1-(2,3-dihydroxy-1-propyl)piperazine, 1-(2-hydroxy-3-phenoxyethyl)piperazine, 1-(2-hydroxy-2-phenyl-1-ethyl)piperazine,

- 25 N,N'-dialkylpiperazines having 1 to 25 carbon atoms in the alkyl group for example 1,4-dimethylpiperazine, 1,4-diethylpiperazine, 1,4-dipropylpiperazine, 1,4-dibenzylpiperazine, 1,4-bis(2-hydroxy-1-ethyl)piperazine, 1,4-bis(2-hydroxy-1-propyl)piperazine, 1,4-bis(2-hydroxy-1-butyl)piperazine, 1,4-bis(2-hydroxy-1-pentyl)piperazine, and 1,4-bis(2-hydroxy-2-phenyl-1-ethyl)piperazine. Other cyclic amines with at least two reactive nitrogen atoms  
30 are melamine and benzimidazoles such as 2-hydroxybenzimidazole and 2-aminobenzimidazole.

### 6.3. Processes

- The reaction between the product containing epichlorohydrin and the alcohol is carried out by any process known in the art such as those described in  
35 US 5,567,359 and US 2006/0079433, the contents of which are incorporated herein by reference.

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The reaction is usually carried out at a temperature between 65 and 90 °C.

Typical molar ratios of alcohol:epichlorohydrin range from 1:1.24 to 1:4.02.

A catalyst is usually used when carrying out the reaction, for instance 5 stannic chloride. The mass ratio of initial alcohol:stannic chloride is generally of 100:0.67.

The duration of the reaction is usually between 0.25 and 1 h.

The epichlorohydrin/alcohol ratio and the duration can be adapted to the required degree of oligomerisation

10 Epichlorohydrin is usually slowly added to the alcohol-catalyst mixture.

The product of the reaction is a monomeric or oligomeric alkyl chloroglyceryl ether.

15 The alkyl chloroglyceryl ether is further converted into an alkyl glycidyl ether by reaction with a basic compound, preferably sodium hydroxide. That reaction is usually carried out with a 35 % aqueous solution of sodium hydroxide at a temperature higher than 90 °C and for a molar ratio alcohol:NaOH of 1:1.5.

20 The alkyl glycidyl ether is further converted into an alkyl glycetyl surfactant by reaction usually with a mixture of sodium bisulfite and sodium sulfite, generally obtained by combining sodium meta-bisulfite with sodium hydroxide.

The reaction between the product containing epichlorohydrin and the amine is carried out by any process known in the art such as those described in US 6,740,633 and US 2006/0052272, the contents of which are incorporated herein by reference.

25 The reaction is usually carried out at a temperature between 25 and 90 °C, in two steps the first one at a temperature between 40 and 60 °C and the second one between 90 and 100 °C.

Typical molar ratios of amine:epichlorohydrin range from 1:1 to 1:1.4.

The duration of the reaction is usually between 0.25 and 1 h.

30 The condensation product between the amine and epichlorohydrin is usually further quaternarized using alkyl halides, epoxides, chloroacetic acid, 2-chloroethanesulfonic acid, chloropropionic acid, epoxysuccinic acid, propane sulfone, 3-chloro-2-hydroxypropanesulfonic acid, dimethyl sulfate and/or diethyl sulfate, or oxidized by oxidation of the tertiary nitrogen atoms of the 35 condensation products to N-oxides.

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#### 6.4. Uses

Examples of detergent ingredients are surfactants or surface deposition enhancing materials. They are usually used as components of cleaning compositions for instance dishwashing, laundry compositions, shampoos and 5 syrbars.

### 7. EPICHLOROHYDRIN ELASTOMERS

#### 7.1. General

The product containing epichlorohydrin according to the invention can be used for the manufacture of epichlorohydrin elastomers.

By epichlorohydrin elastomer, one intends to denote a polymer, containing at least one type of repeat units, at least one type of repeat units containing at least one 2-chloromethylmethoxy group. The polymer can a homopolymer or a copolymer.

Examples of epichlorohydrin elastomers are homopolymers of epichlorohydrin, copolymers of epichlorohydrin with an alkylene or phenylene oxide, and terpolymers of epichlorohydrin with an alkylene or phenylene oxide, and a glycidyl ether.

The alkylene oxide can be selected from styrene oxide, propylene oxide, ethylene oxide, butene-1 oxide, dodecene-1-oxide, and is preferably ethylene oxide.

The glycidyl ether can be selected from alkyl and haloalkyl glycidyl ethers, for instance, 2-chloroethyl glycidyl ether and allyl glycidyl ether.

#### 7.2. Co-reactants

In the application according to the invention, the product containing epichlorohydrin is usually subjected to a reaction with an alkylene or phenylene oxide or with an alkylene or phenylene oxide and a glycidyl ether or the epichlorohydrin is homopolymerized.

#### 7.3. Processes

The reaction is carried out by any process known in the art such as those described in US 3,135,705, US 3,158,580, US 3,158,581, US 3,026,270 and US 3,341,491, the contents of which are incorporated herein by reference.

The reaction is usually carried out in solution in aliphatic or aromatic hydrocarbons, chlorinated hydrocarbons, or ether.

The weight ratio between epichlorohydrin and the alkylene oxide is usually 35 between 20:80 and 90:10.

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The reaction is preferably carried out in the presence of a catalyst formed by reacting  $R^{51}_3Al$  and water (thought to be  $R^{51}_2Al-O-AlR^{51}_2$ ), where  $R^{51}$  can be selected from alkyl, cycloalkyl, aryl or alkaryl radical. The catalyst activity can be improved by the addition of acetylacetone. Some combinations of organozinc and organomagnesium compounds, as well as other additives and chelating agents in combination with alkylaluminum compounds, are also effective catalysts.

5 The reaction can be carried out in a continuous process using a back-mixed reactor.

10 The temperature at which the reaction can be carried out is usually comprised between – 80 °C and 250 °C, preferably between – 80 and 150 °C, more preferably between – 30 and 100 °C. A temperature between 25 and 50 °C is particularly convenient

15 The homopolymer of epichlorohydrin and the copolymers can be further cross-linked, e.g., by further reacting with a polyamine, or an amine in the presence of at least one agent from the group of sulfur, dithiocarbamates, thiuram sulfides and thiazoles, or with a metal compound selected from the group consisting of salts of aromatic carboxylic acids, aliphatic carboxylic acids, carbonic acid, phosphorous acid, silicic acid, and oxides of the metals of  
20 Groups IIA, IIB and IVA of the periodic Table and at least one heterocyclic compound selected from the group consisting of 2-mercaptopimidazolines and 2-mercaptopyrimidine.

#### 7.4. Uses

25 The epichlorohydrin elastomers are generally used in specialty applications, like for instance automotive components ( fuel pump diaphragms, emission control hoses, motor mounts, gaskets, seals and portable fuel tanks), in the aircraft industry, for specialty roofing membranes, coated fabrics, solvent storage containers, paper mill and printing roll and in a variety of oil specialties.— 80 °C and 250 °C, preferably between – 80 and 150 °C, more preferably between  
30 – 30 and 100 °C. A temperature between 25 and 50 °C is particularly convenient

The homopolymer of epichlorohydrin and the copolymers can be further cross-linked, e.g., by further reacting with a polyamine, or an amine in the presence of at least one agent from the group of sulfur, dithiocarbamates, thiuram sulfides.

35 A further goal of the invention is to provide epichlorohydrin which can be used in various applications, obtained from a starting material different from

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propylene. The invention therefore further relates to the use of epichlorohydrin obtained from glycerol in the manufacture of glycidyl amides or glycidyl imides or coagulants or wet-strength resins or cationization agents or flame retardants, or detergent ingredients.

### 5 Examples

Five epichlorohydrin (ECH) samples have been used. Their compositions obtained by gas chromatography analysis are presented in Table 1.

Table 1

Component (g/kg)	ECH 1	ECH 2	ECH3	ECH4	ECH5
acetaldehyde	0.004	n.d.	n.d.	n.d.	n.d.
acrolein	< 0.001	0.003	0.003	n.d.	n.d.
2-propanol	< 0.001	n.d.	n.d.	n.d.	n.d.
3-chloro-1-propene	n.d.	n.d.	n.d.	n.d.	n.d.
allyl alcohol	0.001	< 0.001	< 0.001	n.d.	0.003
hydroxyacetone	0.094	0.018	0.018	0.006	0.006
chloroacetone + (3,3-dichloro-1-propene)	0.033	0.038	0.040	n.d.	0.024
1,2-dichloropropane	0.042	n.d.	n.d.	0.001	n.d.
2,3-dichloro-1-propene	0.005	n.d.	n.d.	0.004	n.d.
1-chloro-2, 3-epoxypropane (*)	> 998.464	> 999.474	> 999.045	> 999.503	> 999.865
1,3-dichloro-1-propene cis maj. + (C <sub>6</sub> H <sub>14</sub> O min.)	0.219	0.008	0.008	0.032	0.004
2-chloro-2-propene-1-ol	0.348	0.016	0.016	0.14	0.012
1,3-dichloro-1-propene trans	0.035	0.010	0.010	0.008	0.009
C <sub>5</sub> H <sub>10</sub> O / C <sub>4</sub> H <sub>7</sub> ClO	n.d.	n.d.	n.d.	0.014	0.001
C <sub>6</sub> H <sub>12</sub> O	n.d.	n.d.	n.d.	0.011	< 0.001
1,3-dichloropropane	0.002	0.34	0.34	0.005	0.030
Cyclopentanone	0.001	0.004	0.004	n.d.	0.004
dibromochloromethane	0.004	n.d.	n.d.	0.084	n.d.
C <sub>6</sub> H <sub>10</sub> O iso 1	0.003	n.d.	n.d.	0.009	< 0.001
C <sub>6</sub> H <sub>10</sub> O iso 2	0.012	n.d.	n.d.	0.009	0.001
1,2-epoxyhexane + (1,2,2-trichloropropane)	0.030	0.002	0.002	n.d.	0.001
C <sub>6</sub> H <sub>10</sub> O iso 3	0.004	n.d.	n.d.	0.031	0.001
dichloroepoxypropane	0.003	n.d.	n.d.	0.006	n.d.

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additions, argon has been introduced in the vessel and tetraoctylammonium bromide and triisobutyl aluminium have been added to the vessel. This addition constituted the time zero of the reaction. After a given time under magnetic stirring at - 30 °C, the reaction has been stopped by adding 1-2 ml of ethanol to the vessel. Half of the volume of the reaction medium has then been submitted to evaporation after which the polymer has been recovered from the vessel.

The conversion has been obtained by comparing the weight of recovered polymer with the weight of added epichlorohydrin.

The theoretical molar weight (Mn th.) has been calculated on the basis of the quantity of tetraoctylammonium bromide.

The measured polymer molar weight (Mn exp) and the molar weight dispersion have been obtained by Gel Permeation Chromatography.

The tacticity of the polymer has been obtained by <sup>13</sup>C and <sup>1</sup>H NMR.

The results of the tests are summarized in Table 3.

15

Table 2

Example n°	ECH (ml)	Toluene (ml)	Noct.Br (ml)	TiBA (ml)
1	4	10.2	2.15	0.71
2	4	10.2	2.15	0.71
3	3.4	9.9	0.91	0.30
4	4	10.2	2.15	0.71
5	4	10.2	2.15	0.71
6	4	11.6	1.08	0.35
7	4	10.2	2.15	0.71
8	4	10.2	2.15	0.71
9	3.6	11.4	0.97	0.43
10	4	11.6	1.08	0.35

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Table 3

Example	Reaction time (h)	Con-version (mol %)	Mn th. (g/mol)	Mn exp. (g/mol)	Dispersion	Tacticity
1	1	100	10000	10700	1.17	atactic
2	1	100	10000	10100	1.23	n.m.
3	2	100	20000	20200	1.17	n.m.
4	1	100	10000	16400	1.22	n.m.
5	1	100	10000	11200	1.20	atactic
6	1	100	20000	77700 (20%) 22200 (80%)	1.40 1.20	n.m.
7	1	80	8000	6800	1.17	n.m.
8	2	95	9500	12100	1.17	atactic
9	2	90	18000	24700	1.18	n.m.
10	6	94	18800	17650	1.17	n.m.

n.m. : not measured

#### Examples 13 to 15 (homopolymerization of ECH)

The tests have been carried out according to the following procedure with 5 epichlorohydrin sample ECH1 (example 13), ECH 2 (example 14) and ECH 3 (example 15). The quantities of chemicals are indicated in Table 4.

The polymerization of epichlorohydrin (ECH) has been carried out in the presence of the system water/triethyl aluminium (TEA).

The procedure of example 1 has been followed except that TEA in solution 10 in toluene and water have been added under argon to the vessel first evacuated and dried, left under magnetic stirring under vacuum for 30 min, before ECH in toluene has been added (time zero of the reaction). The polymerization has been carried out at a temperature of 25 °C for 12 h. The results have been summarized in Table 5

Table 4

Example n°	ECH (ml)	Toluene (ml)	H <sub>2</sub> O (μl)	TEA (ml)
13	4	10	23	0.67
14	4	10	23	0.67
15	4	10	23	0.67

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Table 5

Example	Reaction time (h)	Conversion (mol %)	Mn exp. (g/mol)	Dispersion	Tacticity
13	12	47	216000	2.02	n.m.
			7000	1.04	
14	12	50	285200	3.51	atactic
			5850	1.08	
15	12	55	357600	3.45	atactic
			8100	1.31	

n.m. : not measured

Example 16

Preparation of a product consisting predominantly in diglycidyl diether of Bisphenol A according to US 2,811,227

The apparatus employed was a thermostatised flask equipped with a mechanical stirrer, with a jacket containing a thermocouple and with a Dean-Stark separator surmounted by a water-cooled condenser. A pump was used to inject a caustic soda aqueous solution at a constant rate in the flask.

The reaction flask was initially charged with a mixture of bisphenol A (68.4 g, 0.3 mol) and the epichlorohydrin sample ECH4 coming from a propylene-chlorine plant (277.5 g, 3.0 mol). The analysis of the epichlorhydrin is given in Table 1. The trichloropropane content is of 0.049 g/kg. The mixture was heated at reflux under stirring to a temperature of 111°C. A 40 % aqueous solution of caustic soda (60.8 g, 0.6 mol) was introduced at a rate of 12 ml/h during 3.5 hour. The temperature of the mixture in the flask was maintained in the range 100 °C - 115 °C in order to assure a constant reflux. The epichlorohydrin rich organic phase decanted during the reaction as a lower phase in the separator was recycled regularly in the reaction flask and the aqueous rich phase collected as an upper phase in the separator was regularly drawn off. The heating was maintained for 15 min after the total introduction of the caustic soda solution to achieve the collect of the water phase in the decantor. 29.7 g of aqueous phase was collected with a composition given in Table 6.

The epichlorohydrin in excess was removed from the reaction mixture by distillation under a vacuum of 30 mbar and by a progressive heating of the mixture to 109°C. 156.1 g (1.7 mol) of epichlorohydrin was recovered in this step. The composition of the distillate is given in Table 6.

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The salt was separated from the crude product (45.5 g) after addition of 567.2 g of toluene under agitation and by filtration. The cake of filtration was washed with 124.4 g of toluene. The toluene solutions were mixed and evaporated at 185°C under a pressure of 1 mbar.

5        659.4 g of toluene was recovered as the condensate of the evaporated fraction with a composition given in Table 6. The residual product of the evaporation (100.5 g) contained the diglycidyl ether of bis-phenol A as a major product and no trace of unconverted bis-phenol A (< 5 mg/kg). The residue contained 4.98 mol epoxy per kg and 1.52 % of hydrolysable chlorine.

10      Example 17

The trial was realized in the apparatus described in example 16.

15      The reaction flask was initially charged with a mixture of bisphenol A (68.4 g, 0.3 mol) and epichlorohydrin sample ECH 5 (277.5 g, 3.0 mol). The analysis of the epichlorohydrin is given in Table 1. The trichloropropane content is of 0.007 g/kg. The mixture was heated at reflux under stirring to a temperature of 119°C. A 40 % aqueous solution of caustic soda (60.8 g, 0.6 mol) was introduced at a rate of 12 ml/h during 3.5 hour. The temperature of the mixture in the flask was maintained in the range 102 °C – 119 °C in order to assure a constant reflux. The epichlorohydrin rich organic phase decanted during the 20     reaction as a lower phase in the separator was recycled regularly in the reaction flask and the aqueous rich phase collected as an upper phase in the separator was regularly drawn off. The heating was maintained for 15 min after the total introduction of the caustic soda solution to achieve the collect of the water phase in the decantor. 54.5 g of aqueous phase was collected with a composition 25     given in Table 6.

The epichlorohydrin in excess was removed from the reaction mixture by distillation under a vacuum of 30 mbar and by a progressive heating of the mixture to 118°C. 148.2 g (1.5 mol) of epichlorohydrin was recovered in this step. The composition of the distillate is given in Table 6.

30      The salt was separated from the crude product (47.8 g) after addition of 228.4 g of toluene under agitation and by filtration. The cake of filtration was washed with 97.3 g of toluene. The toluene solutions were mixed and evaporated at 180°C under a pressure of 1 mbar.

35      305.0 g of toluene was recovered as the condensate of the evaporation with a composition given in Table 6. The residual product of the evaporation (99.8 g) contained the diglycidyl ether of bis-phenol A as a major product and no trace of

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unconverted bis-phenol A (< 5 mg/kg). The residue contained 4.93 mol epoxy per kg and 0.49 % of hydrolysable chlorine.

The High Performance Liquid Chromatography analyses of the residual products obtained in examples 16 and 17 are similar.

Component	Example 16	Example 17
C <sub>2</sub> H <sub>6</sub> O iso 2	0.040	0.31
1,2-epoxyhexane + (1,2,2-trichloropropane)	n.d.	n.d.
C <sub>2</sub> H <sub>6</sub> O iso 3	0.036	0.21
dichlorepoxypropane	0.006	n.d.
1,3,3-trichloro-1-propene cis + 1,1,3-trichloropropene	0.006	n.d.
1,1,2-trichloropropene	0.005	n.d.
chlorobenzene	0.001	n.d.
1,2,3-trichloro-1-propene trans	0.069	n.d.
1,2,3-trichloropropene trans	0.003	n.d.
1,3-dichloro-2-propanol	3.4	143
1,2,3-trichloropropane	0.022	n.d.
1,2,3-trichloropropene cis	n.d.	n.d.
3-chloro-1,2-propanediol + 2,3-dichloro-1-propanol	0.13	5.9
C <sub>2</sub> H <sub>11</sub> Br	n.d.	<0.05
C <sub>6</sub> H <sub>10</sub> Ch iso 1	0.009	n.d.
C <sub>6</sub> H <sub>10</sub> Ch iso 2	0.007	n.d.
methyl glycidyl ether	n.m.	n.m.
Unknowns (sum)	0.299	10.00
	1.31	0.213
		1.3
		1.373

n.d. : not detected, n.m. : not measured

Example 18

A glass thermostated jacketed reactor having a working volume of 305 ml was supplied continuously with 47.2 wt% sodium hydroxide and with an aqueous mixture of dichloropropanol, a mixture prepared from glycerol and concentrated hydrochloric acid in the presence of an organic acid according to the International Application WO 2005/054167 filed by Solvay SA. The mixture contained 575 g of water/kg, 404.6 g of 1,3-dichloro-2-propanol/kg, 20.1 g of 2,3-dichloro-1-propanol/kg, 0.14 g of acrolein/kg, 0.13 g of epichlorohydrin/kg, 0.04 g of 1,2,3-trichloropropene/kg, 0.04 g of chloroacetone/kg and 0.03 g of an ether of crude formula  $C_6H_{10}O_2Cl_2/kg$ . The sodium hydroxide was introduced at a flow rate of 262 g/h and the aqueous dichloropropanol mixture was introduced at a flow rate of 1180 g/h. The reaction medium was constantly maintained at 25°C with vigorous stirring. The liquid mixture exiting the reactor by continuous overflow was collected and then separated in batch mode in a glass funnel so as to obtain a first separated fraction and a second separated fraction. 3753 g of first separated fraction (MEL1) were subjected to a batch distillation under a vacuum of 193 mbar. The batch distillation was carried out using a round-bottomed flask equipped with a magnetic stirrer bar, a thermocouple to measure the temperature of the liquid and a plate distillation column surmounted by a device enabling part of the distillate to be refluxed at the top of the column. The glass plate column comprised 5 plates having a diameter of 30 mm, pierced by an internal aperture 10 mm diameter central hole for the flow of liquid and three rows of small holes having a diameter of around 0.8 mm, spaced at regular intervals of less than 1 mm between each hole, placed in an arc over three quarters of the circumference. The spacing between the plates was 30 mm. The column was adiabatic (glass jacket under vacuum). A thermocouple placed in the top of the distillation column enabled the temperature of the gas phase distilled to be measured. The distillate was collected in a funnel with a stopcock. A first distillation fraction was collected between 49°C and 67°C and gave, after separation, 425 g of an organic phase (D1 org) and 159 g of an aqueous phase (D1 aq). The organic phase (D1 org) was combined with the contents of the boiler to give the mixture (MEL2) which was then distilled at a temperature of 187°C. A second distillation fraction was collected between 66°C and 67°C and resulted, after separation, in 244 g of an organic phase (D2 org) and 11.5 g of an aqueous phase (D2 aq). A main distillate of 2082 g of epichlorohydrin at 999.5 g/kg was then collected (D3) at a temperature of 67°C. The mixture

constituting the final boiler (MEL3) weighed 1226 g and only contained a very low fraction of epichlorohydrin implemented. The organic phase D2 org and the boiler MEL3 could be recycled to the distillation operations in order to recover, for enhanced value, epichlorohydrin and a mixture of 1,3-dichloro-2-propanol 5 and 2,3-dichloro-1-propanol respectively. The compositions (g/kg) used and obtained in the distillation operations are described in Table 7.

Table 7

	MEL1	D1 org	D1 aq	MEL2	D2 org	D2 aq	D3	MEL3
1,2,3-Trichloropropane	0.16	n.d.	n.d.	0.018	n.d.	n.d.	n.d.	0.015
2,3-Dichloro-1-propanol + 3-chloro-1,2-propanediol	56	1.94	36.42	61	0.046	21	n.d.	174
Phenol	0.011	n.d.	n.d.	0.012	n.d.	n.d.	n.d.	0.035
C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>	< 0.005	n.d.	n.d.	< 0.005	n.d.	n.d.	< 0.01	0.008
C <sub>6</sub> H <sub>12</sub> OCl <sub>2</sub>	0.056	n.d.	n.d.	0.060	n.d.	n.d.	n.d.	0.051
3,5-Dimethyl-2-cyclohexen-1-one	0.011	n.d.	n.d.	0.012	n.d.	n.d.	n.d.	0.035
C <sub>6</sub> H <sub>9</sub> Cl <sub>3</sub> O <sub>2</sub>	0.031	n.d.	n.d.	0.034	n.d.	n.d.	n.d.	0.102
1-Phenoxy-2-propanone	0.88	n.d.	n.d.	0.078	n.d.	n.d.	n.d.	1.754
C <sub>6</sub> H <sub>10</sub> Cl <sub>2</sub> O <sub>2</sub>	0.076	0.002	n.d.	0.101	n.d.	n.d.	n.d.	0.325
C <sub>9</sub> H <sub>9</sub> Cl <sub>3</sub>	< 0.005	n.d.	n.d.	< 0.005	n.d.	n.d.	n.d.	0.012
C <sub>6</sub> H <sub>11</sub> O <sub>2</sub> Cl <sub>3</sub>	0.74	n.d.	n.d.	0.81	n.d.	n.d.	n.d.	2.95
C <sub>9</sub> H <sub>15</sub> O <sub>2</sub> Cl <sub>2</sub> +C <sub>9</sub> H <sub>11</sub> O <sub>4</sub> Cl <sub>3</sub>	< 0.005	n.d.	n.d.	< 0.005	n.d.	n.d.	n.d.	0.56
Sum of unknowns	0.27	0.07	0.16	0.31	0.08	n.d.	n.d.	1.07
Methyl glycidyl ether	0.02	n.d.	0.03	0.03	n.d.	n.d.	0.04	
H <sub>2</sub> O	37	14.0	n.d.	2.32	9.9	n.d.	0.32	0.33

n.d. = not detected

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CLAIMS

1 - Product containing epichlorohydrin and trichloropropane, wherein the amount of trichloropropane is of less than 0.01 g of trichloropropane per kg of product.

5        2 - Product according to Claim 1, containing in addition at least one or more of the following compounds:

(A) halogenated hydrocarbon compounds different from trichloropropane chosen from chloropropene, trichloropropene, chloropropanol, chloropropenol, dichloropropene, dichloropropane, dichloropropanol,

10      monochloropropanediol, chloroethers, monochlorobenzene, and any mixture of at least two of them, and/or

(B) compounds chosen from acrolein, methyl glycidyl ether, chloroacetonc, glycerol, hydroxyacetone, glycidol, cyclopentanone and any mixture of at least two of them.

15      3 - Product according to Claim 1 or 2, wherein the trichloropropane is chosen from 1,2,3-trichloropropane, 1,1,1-trichloropropane, 1,1,3-trichloropropane, 1,1,2-trichloropropane and any mixtures of at least two of them.

20      4 - Product according to any one of Claims 1 to 3, containing more than 900 g of epichlorohydrin per kg of product.

5        5 - Process for manufacturing the product according to any one of Claims 1 to 4, comprising the following steps:

25      a) in a liquid reaction medium, a mixture of dichloropropanol containing 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol, in which the 1,3-dichloro-2-propanol content, relative to the sum of the 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol contents, is at least 10 wt%, is reacted with at least one basic compound in order to form epichlorohydrin and at least one salt; and

30      b) at least one part of the liquid reaction medium from step a) is subjected to a settling operation in which a first fraction containing most of the

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epichlorohydrin which was contained in the part of the reaction medium from step a) before the settling operation is separated from a second fraction containing most of the salt which was contained in the part of the reaction medium from step a) before the settling operation; and

- 5    c) the first fraction separated in step b) is subjected to at least one supplementary treatment chosen from dilution, concentration, evaporation, distillation, stripping, liquid/liquid extraction and adsorption operations, alone or in combination.

6 - Process according to Claim 5, in which the reaction from step a) is  
10    carried out in at least two reaction zones, in which the volumes are assembled in a single jacket, and in which each of the reaction zones is supplied with the dichloropropanol mixture and/or with the basic compound.

7 - Process according to Claims 5 or 6, in which, in step c), the first fraction separated in step b) is subjected to at least one of the treatments chosen from:

- 15    • a treatment comprising at least one liquid/liquid extraction operation with an aqueous composition, and in which a first part containing most of the epichlorohydrin which was contained in the first fraction separated in step b) before the extraction operation, is separated from a second part containing most of the water;
- 20    • a treatment comprising at least two distillation operations, of which at least one is an operation for drying by azeotropic distillation, and, at the end of the treatment, at least a first portion containing most of the epichlorohydrin which was contained in the first fraction before the distillation operations is obtained; and
- 25    • a treatment which comprises at least one adsorption operation and at least one distillation operation, and, at the end of the treatment, at least a first cut containing most of the epichlorohydrin which was contained in the first fraction before the treatment is obtained.

8 - Process according to any one of Claims 5 to 7, in which the first fraction separated in step b) contains dichloropropanol and said fraction is subjected to at least one of the treatments chosen from:

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- a treatment comprising at least one liquid/liquid extraction operation with an aqueous composition, and in which a first part containing most of the epichlorohydrin which was contained in the first fraction separated in step b) before the extraction operation, is separated from a second part containing most of the water;
- a treatment comprising at least two distillation operations, preferably at least two distillation operations of which at least one is an operation for drying by azeotropic distillation, and, at the end of the treatment, at least a first portion containing most of the epichlorohydrin which was contained in the first fraction before the distillation operations, and at least a second portion containing most of the dichloropropanol which was contained in the first fraction before the distillation operations, are obtained; and
- a treatment which comprises at least one adsorption operation and at least one distillation operation, and, at the end of the treatment, at least a first cut containing most of the epichlorohydrin which was contained in the first fraction before the treatment, and at least a second cut containing most of the dichloropropanol which was contained in the first fraction before the treatment, are obtained.

9 - Use of the product according to any of claims 1 to 4 in the manufacture  
20 of epoxy resins or glycidyl esters or glycidyl ethers or glycidyl amides or  
glycidyl imides or coagulants or wet-strength resins or cationization agents or  
flame retardants or detergent ingredients or epichlorohydrin elastomers.

10 - Use according to claim 9 wherein the product containing  
epichlorohydrin is subjected to a reaction with a compound containing at least  
25 one active hydrogen atom, selected from monoalcohols, monocarboxylic acids,  
polyols, polyamines, amino alcohols, polyimides and amides, polycarboxylic  
acids, and mixtures thereof, in order to obtain an epoxy resin or a glycidyl ether  
or a glycidyl ester or glycidyl amides or glycidyl imides.

11 - Use according to claim 9 wherein the product containing  
epichlorohydrin is reacted with ammonia, an amine, a polyaminoamide or a  
polyimine in order to obtain a coagulant, or wherein the product containing  
epichlorohydrin is reacted with a polyamine, a polyamide or a polyaminoamide  
in order to obtain a wet-strength resin, or wherein the product containing

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epichlorohydrin is reacted with an amine, an amine salt, or a mixture thereof in order to obtain a cationization agent.

12 - Use according to claim 9 wherein the product containing epichlorohydrin is reacted with a compound selected from phosphoric acid, a

- 5 phosphoric acid salt, a phosphorus oxychloride, a phosphoric acid ester, a phosphonic acid, a phosphonic acid ester, a phosphonic acid salt, a phosphinic acid, a phosphinic acid ester, a phosphinic acid salt, a phosphine oxide, a phosphine, or a mixture thereof, in order to obtain a flame retardant.

13 - Use according to claim 9 wherein the product containing

- 10 epichlorohydrin is reacted with a monoalcohol containing from 12 to 16 carbon atoms or an ethoxylated alcohol or with an amine selected from the group consisting of linear alkylamines, branched alkylamines, cycloalkylamines, alkoxyamines, amino alcohols, cyclic amines containing at least one nitrogen atom in a ring structure, alkylenediamines, polyetherdiamines, 15 polyalkylenepolyaminesamine in order to produce a detergent ingredient.

14 - Use according to claim 9 wherein the product containing epichlorohydrin is reacted with an alkylene or phenylene oxide or with an alkylene or phenylene oxide and a glycidyl ether or homopolymerized in order to obtain an epichlorohydrin elastomer.

- 20 15 - Use of epichlorohydrin obtained from glycerol in the manufacture of glycidyl amides or glycidyl imides or coagulants or wet-strength resins or cationization agents, or flame retardants, or of detergent ingredients.

Fig. 1

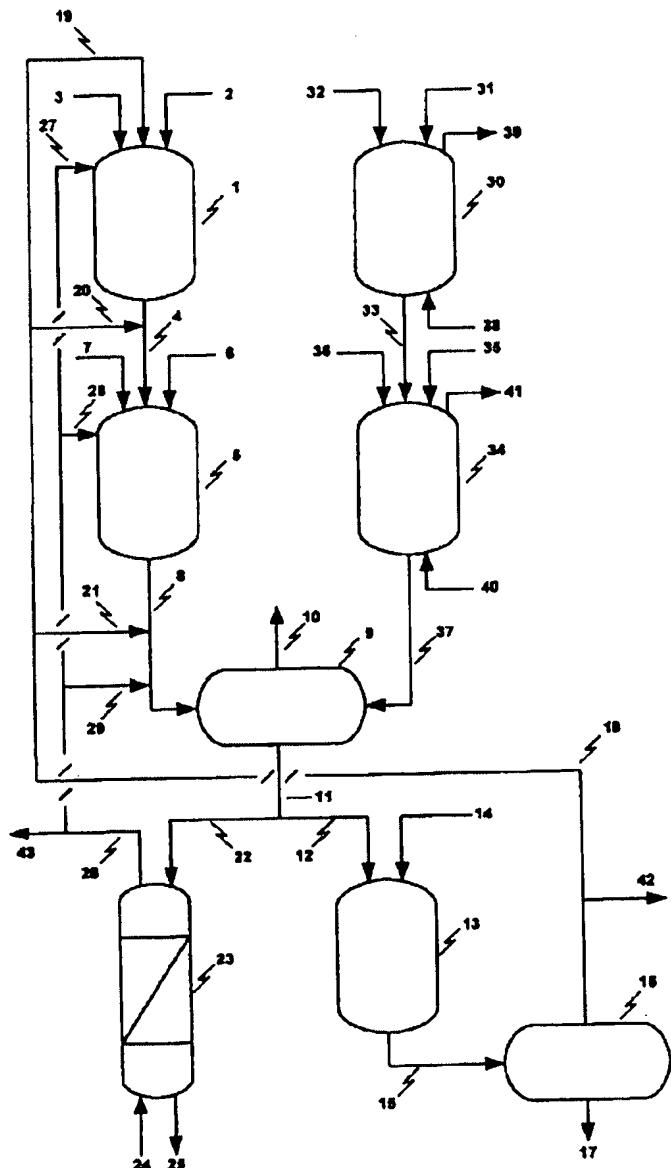


Fig. 2

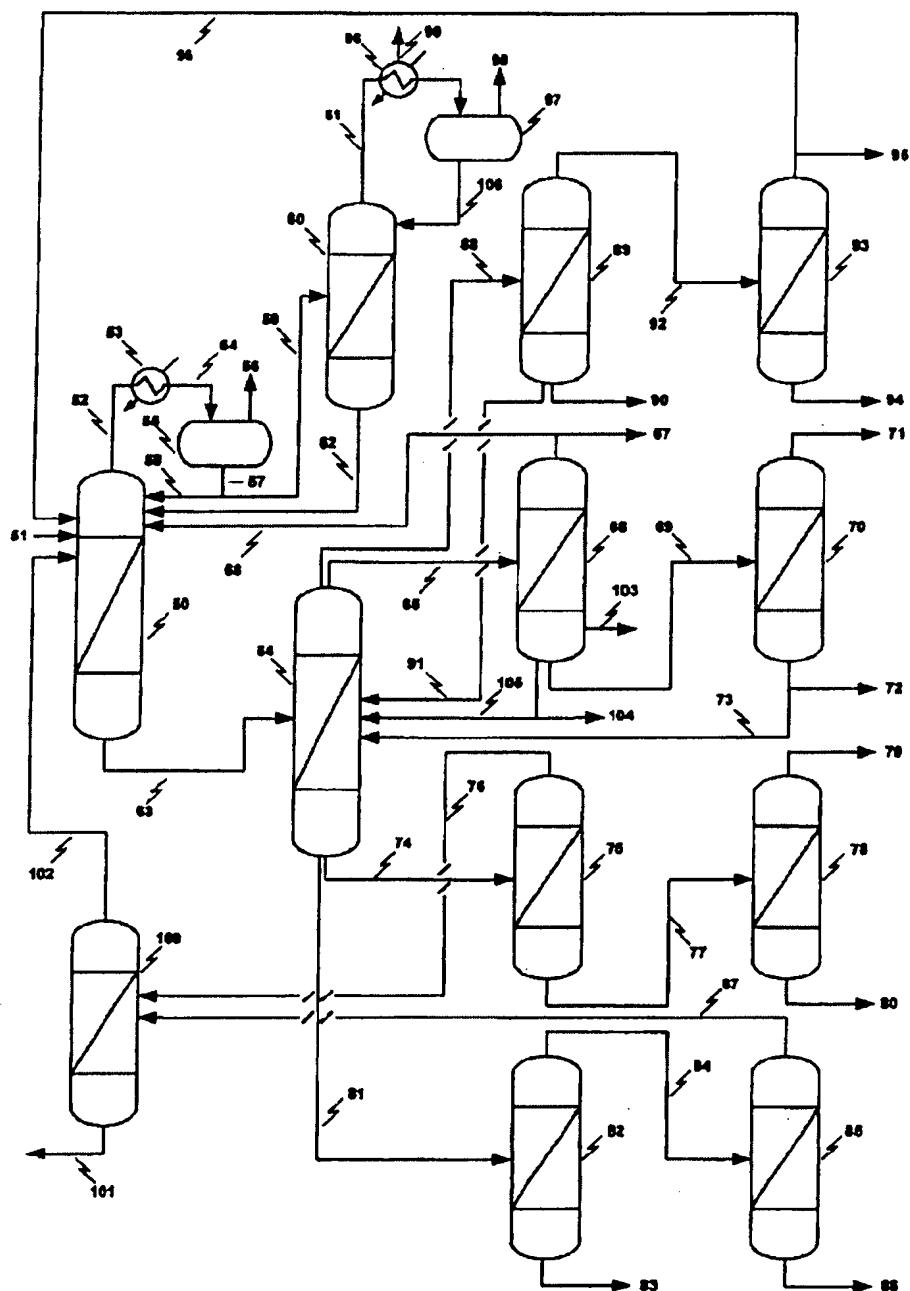


Fig. 3

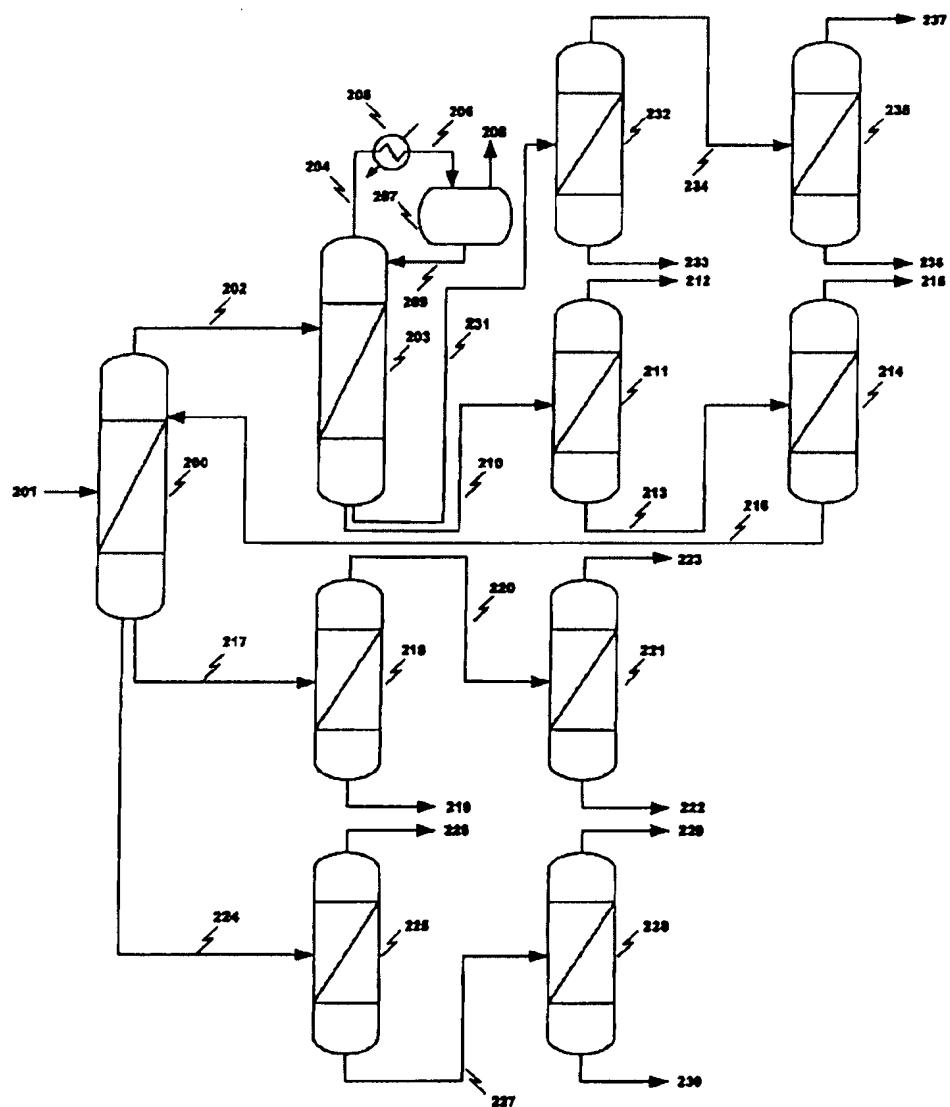


Fig. 4

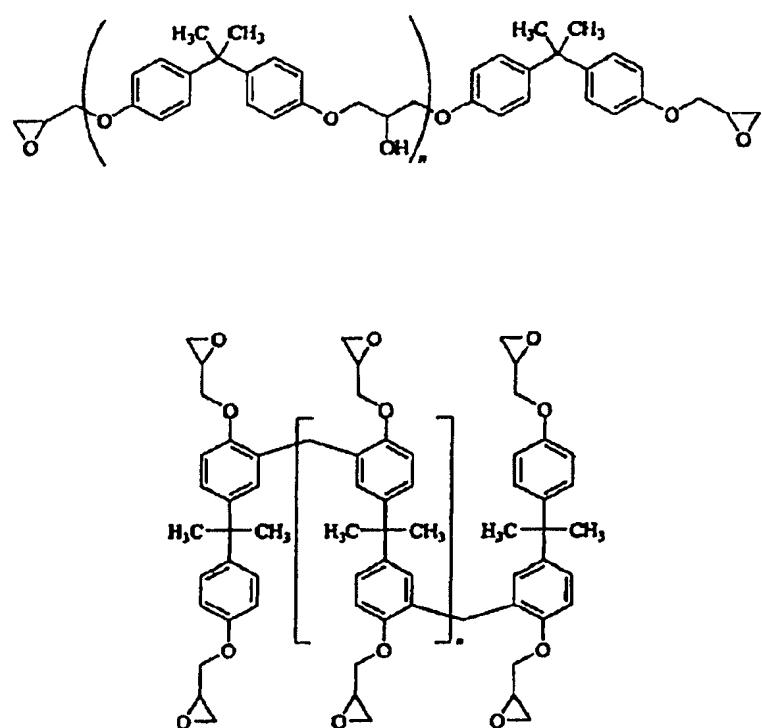


Fig. 5

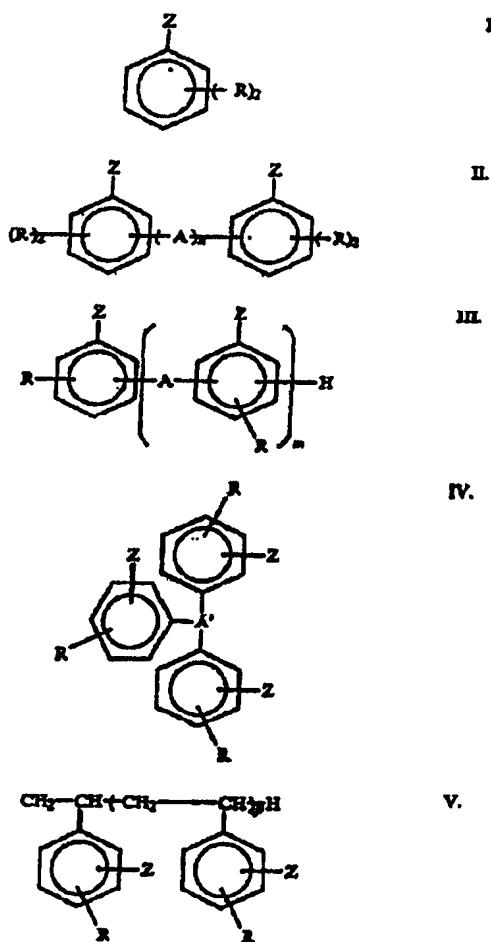


Fig. 6

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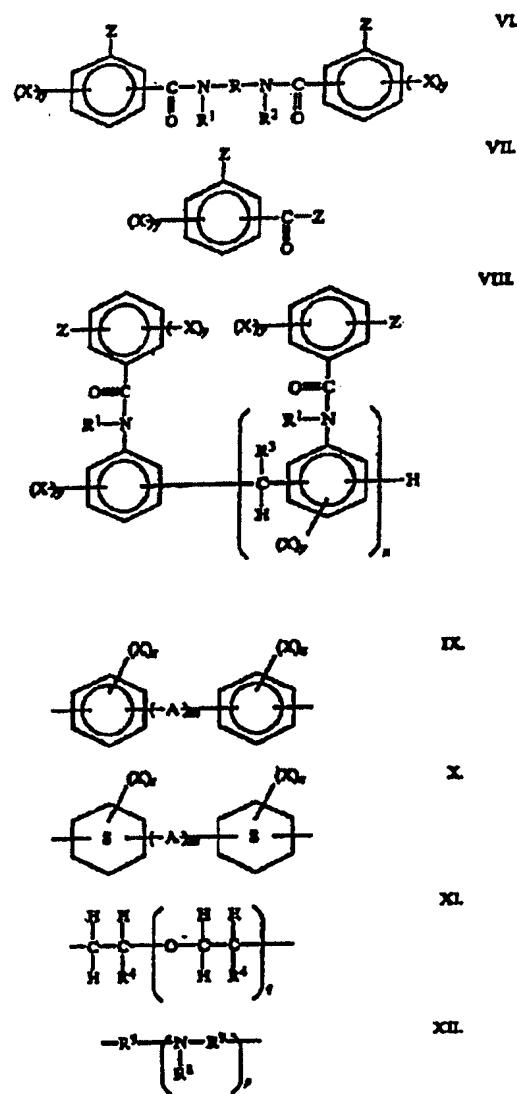


Fig. 7

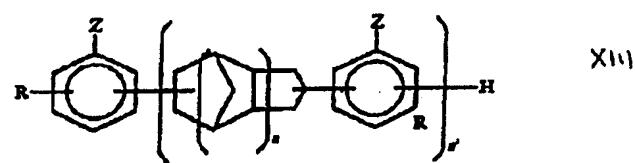


Fig. 8

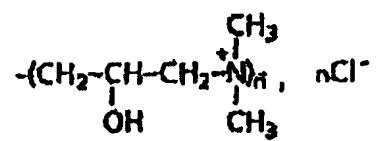


Fig. 9

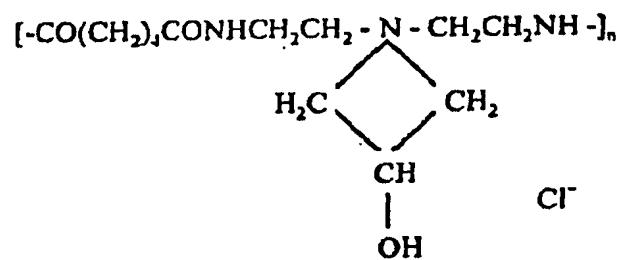
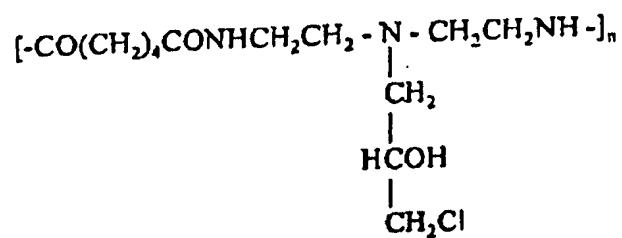
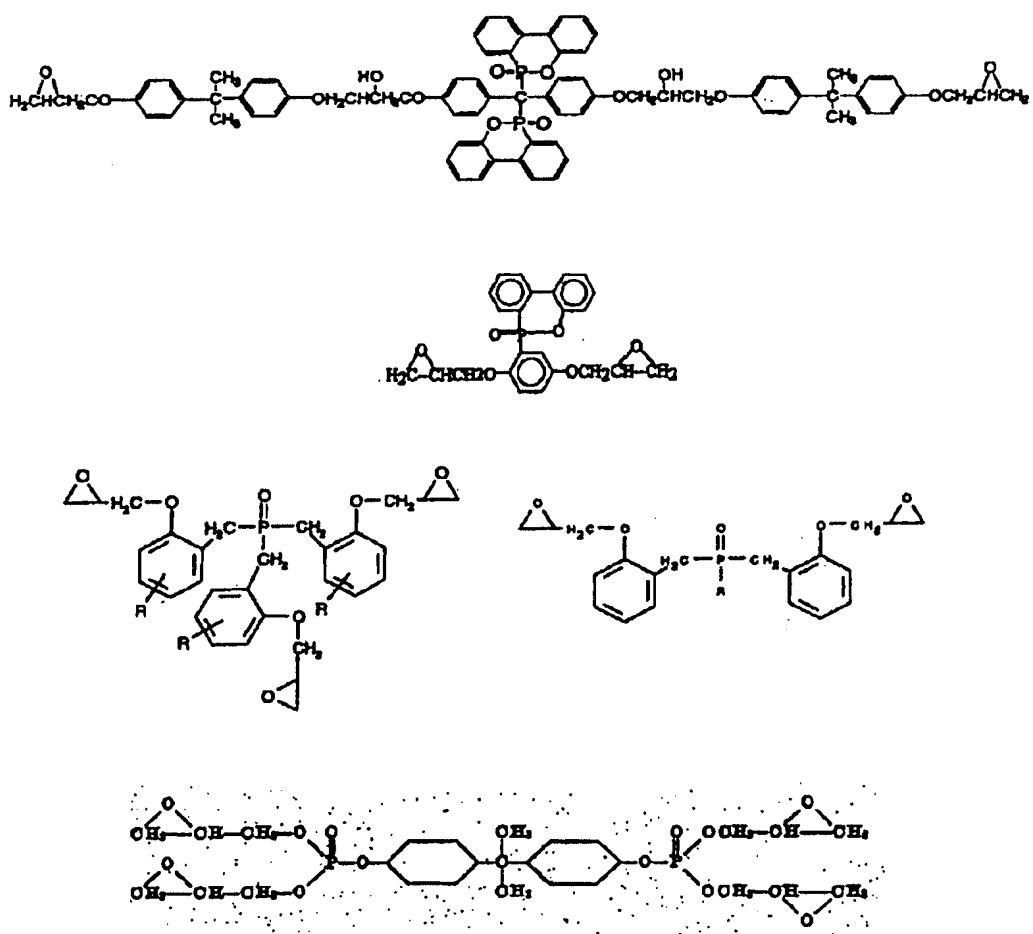


Fig. 10



**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/EP2008/057247

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. C07D303/08		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) C07D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, CHEM ABS Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 885 903 A (SOLVAY [BE]) 24 November 2006 (2006-11-24) page 2, line 32 – page 3, line 19 page 6, lines 1-5 claims 2,11-13 page 1, lines 3-20 -----	1-15
X	GB 2 173 496 A (INST CIEZKIEJ SYNTEZY ORGANIKI ZACHEM ZAKLADY CHEMIC) 15 October 1986 (1986-10-15) claims 1-5 page 1, line 65 – page 2, line 20 page 2; example II -----	1-15
		-/-
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.		<input checked="" type="checkbox"/> See patent family annex.
* Special categories of cited documents: *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the International filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the International filing date but later than the priority date claimed		
*T* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
8 September 2008		16/09/2008
Name and mailing address of the ISA/ European Patent Office, P.B. 5016 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 apo nl, Fax. (+31-70) 340-3016		Authorized officer  Marzi, Elena

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2008/057247

## C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 919 551 A (SOLVAY [BE]) 2 June 1999 (1999-06-02) claims 1-9 column 1, paragraph 3-7 column 4, paragraph 27-29 column 6, paragraph 41 column 8, paragraph 56 _____	1-15
X	EP 1 059 278 A (SHOWA DENKO KK [JP]) 13 December 2000 (2000-12-13) page 6, paragraphs 57,58 claim 12 page 2, paragraph 2 _____	1-15

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International application No

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